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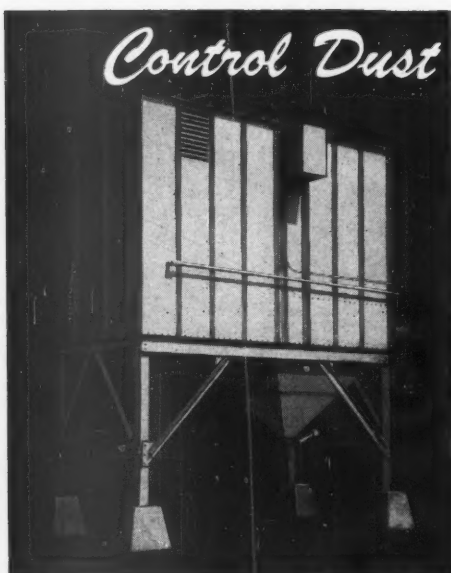
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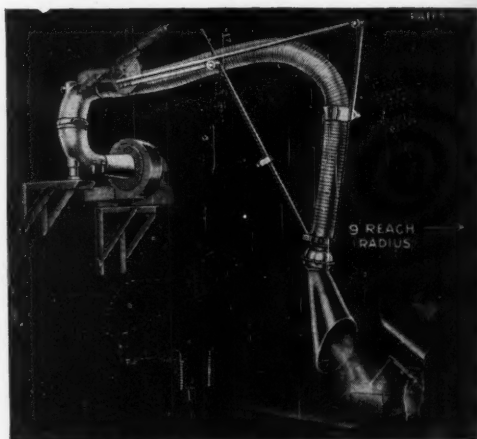
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Threshold Limits

—A Panel Discussion

Moderator: JAMES H. STERNER, M.D., Medical Director
Eastman Kodak Company, Rochester, New York

THE CONCEPT of the "threshold limit" is the most important single factor influencing present day industrial hygiene practice. The past few decades have witnessed a transition from a mere postulate that an exposure to an industrial toxin could be controlled by limiting the concentration to a specific "safe" level to the present wide acceptance and application of maximum allowable concentration values for an ever increasing number of commonly encountered hazardous industrial agents.

As experience has demonstrated the utility and reliability of threshold limits in the hygienic control of the industrial environment, there has been a greater emphasis on the role of the analyst and the engineer in the routine industrial hygiene activities. The earlier fears expressed by some physicians that an increasing reliance on non-medical control methods would have unfortunate results, have not been realized. This does not mean that the role of the physician in defining threshold limits has diminished. On the contrary, a greater participation by the physician, from the development of the initial medical data to the final testing of a postulated maximum allowable concentration value by prolonged clinical evaluation of workers exposed in actual work conditions, is essential if the limits are to have the reliability and authority which will permit the safe application of environmental controls. It cannot be emphasized too strongly, that the final proof of the effectiveness of the program based on threshold limits,

must rest upon a repeated, comprehensive, and thorough medical examination.

Early in the evolution of the threshold limit concept, and still repeated on occasion, an objection was raised that the factor of individual susceptibility would seriously limit, if not actually negate, the application of the principle. If the limits were based on human lethal dose curves—and even though some point far down on the toe of the typical cumulative fatal dose curve were selected, the objection might be valid. What is not clearly recognized is that for a particular substance, the maximum allowable concentration figure is related to a less serious response than lethality, and that usually this selected function is sufficiently lower than the lethal dose curve that there is no practical overlap.

SUCH A CURVE may define the relationship to a symptom such as nausea, or upper respiratory tract irritation, or some other factor which should be easily reversible and not closely followed by a serious reaction.

Even here, the 50 percentile point should not be selected, but some significantly lower figure which will insure that all but the exceptional industrial worker can work safely and with reasonable comfort. We know, of course, that we are still a long way from this ideal, but the defect is not in the principle, but in our lack of knowledge and ability to define the limits with sufficient accuracy. The concept of "allergy" has been interjected in many instances where there is not the slightest evidence to support such an action, qualitatively or quantitatively. Not infrequently the "individual susceptibility" objection is based on

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confused or sloppy thinking, or is interposed in a specific case to support a cause which is otherwise untenable.

A legitimate criticism, and one which as yet has not been answered adequately, is the relative inequality of threshold limit values. The factor of safety between the limit and the level which may cause a serious effect may be relatively narrow for one agent, such as carbon tetrachloride, or have a wide margin for another agent, as in the case of acetone.

Similarly, the single threshold limit does little to define the relative hazard of substances with respect to acute or chronic effects—with benzene and carbon tetrachloride as references. Still another factor is the disparity of the information upon which limits are based. In a few instances there is reliable clinical information, developed on a relatively large group of exposed persons and over many years. This contrasts with the values predicated chiefly on animal experimentation, with little opportunity for prolonged and thorough clinical test. These factors are well appreciated by the skilled industrial hygienist, but they may not be immediately apparent to the less experienced person who has reason to consult a table of threshold limits.

In spite of these defects, the value and importance of threshold limits will increase materially. There is no other mechanism which will so effectively permit us to transfer the experience gained in one situation with an industrial toxin to another. We must admit the limitations of our present values, but in doing this we emphasize the paucity of our present information, not the failure of the principle.

All of us recognize that there are no obvious or easy answers to the criticisms which have been raised as to the limitations in applying threshold limits. From my personal experience in guiding a diversified industrial hygiene program, I am most grateful for the threshold limits which others have contributed, and I am certain that the benefit of their experience has enabled us to give our workmen a safer, more healthful, and happier life.

In the following series of discussions, we shall take a look at the present status of our threshold limit activity in each of the major categories, solvents, dusts, gases, and

metal fumes. Perhaps we can today move closer to the goal of greater reliability and effectiveness for these most useful criteria.

Organic Vapors

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THE TERM "threshold limit" is used in the field of industrial hygiene to describe the concentration of an atmospheric contaminant which should cause no significant injury to the health of the large majority of persons even after repeated daily exposure. The assignment of threshold limit values, or "bench marks," to certain hazardous materials has been made possible through the work of research laboratories of industry, universities and government, and by information secured during environmental studies in which the results of field and laboratory determinations are correlated with clinical signs and symptoms. Constant improvement and new developments in instrumentation, air sampling techniques and analytical methods have gone far in transforming what have sometimes been referred to as "guesstimates" into rather intelligent estimates. In addition to these new developments and refinements in analytical methods, the examination of body fluids for contaminants or their metabolites is playing an increasingly important role in providing accurate threshold limit data.

For some time, the measurement of carbon disulfide, metals and some of the alcohols in body fluids has been used as an index of absorption and exposure, as has the ratio of inorganic to total sulfates in the urine as a measure of benzene absorption and exposure, and the formation of carboxyhaemoglobin in the case of carbon monoxide. More recently, data have been made available showing the relationship between body fluid concentrations of hippuric acid and toluol exposure, trichloroacetic acid in chlorinated hydrocarbon exposures, par-nitrophenol for measuring parathion absorption, thiocyanates for cyanides, salts of glucuronic acid for some of the esters,

alcohols and ketones, porphyrins for metals, etc. It is indeed encouraging to observe the growth of new information which can be used effectively in the development of threshold limit data, and to note the change which has occurred in less than 25 years. Many of you will remember the time when very few dependable methods were available for efficient air sampling and when threshold limit values were practically unknown quantities, except for such materials as lead, carbon monoxide, chromic acid and some dusts of known free-silica content.

As the development of more and more information continues, the need for periodic re-examination and reappraisal of threshold limit values becomes more apparent and important. It is of interest, for example, to recall that prior to the intensive laboratory and field study reported by Smyth and his associates in 1936, an average concentration of 1000, or even 1600, parts of carbon tetrachloride vapor per million parts of air was considered reasonably safe for repeated daily exposure. It was not so long ago that prolonged exposure to benzene vapor at levels in the vicinity of 100 parts per million were generally believed to cause no appreciable injury to health. Careful study and continued experience with the use of these solvents indicated the need for reducing their threshold limit values if the health of exposed persons was to be adequately protected. On the other hand, research and further experience with other solvents such as acetone, methanol, trichloroethylene and perchloroethylene have provided data which justified the upward revision of threshold limit values for these materials. It seems reasonable to believe that such changes will continue so long as new and more accurate information on the toxicology of organic chemicals is developed. The scope of the problem is staggering when we consider the vast array of new organic compounds being adapted to industry and agriculture. In reply to the question, which is often asked, "Are present threshold limit values adequate?" the answer is that the adequacy of these values is entirely dependent upon the accuracy and availability of toxicological data and industrial experience. We shall always be able to add to our knowledge on this subject.

At the present time, there is considerable

research in progress which should add to our understanding of the toxic action of the newer organic insecticides. Laboratory work and field studies in this country and in Canada are adding to our information on parathion, DDT, chlordane and others. Research work is underway in a number of industrial hygiene laboratories to investigate further possibilities in the correlation of concentrations of contaminants and metabolites in body fluids with physiological symptoms and atmospheric concentrations. The larger industries are giving increased attention to the study of possible toxic properties of new organic chemicals and industrial products during the course of development and prior to full-scale production. The Public Health Service is doing considerable toxicological work on the investigation of materials of interest to our armed forces. Industrial hygiene units throughout the country are conducting studies of on-the-job exposures in industry each year. Benzpyrene and other commonly occurring materials of suspected carcinogenic importance undoubtedly will receive considerable attention during the next few years. Results of these projects and other research will add immeasurably to the fund of data which can be used in the reappraisal of existing threshold limit values and in the development of new ones.

LAST YEAR, the Committee on Threshold Limits of the American Conference of Governmental Industrial Hygienists presented bibliographic material covering 50 of the contaminants listed in the 1953 table of values. This year, few changes were made in the former list, but 37 new materials have been presented as "Tentative Threshold Limit Values," being set apart from the original list because of the lesser certainty associated with the values assigned. The addition of this tentative list was considered desirable for the following reasons: (1) It is felt that a need exists for such a list. (2) Tentative values, even though they may be based on limited information, are felt to provide at least general guidance in the control of exposure. (3) Long intervals often elapse between the development of the first experimental data and its practical industrial experience from which past values have frequently been obtained. (4) The

tentative list may serve as a "clearing house" until such time as these values are more definitely established. All new values will be placed on this tentative list before their appearance on the list of values adopted by the American Conference of Governmental Industrial Hygienists. It is hoped that this procedure will avoid undesirably frequent changes in the established list.

The committee, in presenting this tentative list, realizes that documentation in many cases is extremely limited and therefore welcomes additional information on experience with any of the materials listed and comments on the suggested values.

Though it was mentioned earlier that present threshold limit values are by no means adequate, it is apparent that, over the years, there has been a considerable accumulation of toxicological data which has contributed to the accuracy of values now in use.

Further additions to the number and accuracy of values will depend upon the continued cooperation of industry, universities, and government and upon further on-the-job experience and investigation in the use of both old and new materials. We cannot afford to take a firm stand that there is only one way, or that any one method is better than all others, in the evaluation of the severity of a potentially hazardous exposure. Many of the threshold limit values now in use, which have stood the test of time, are those which were established by the accumulation of data on atmospheric concentrations, measurement of contaminants in body fluids and by careful observation of physiological symptoms.

Just as important perhaps as the establishment of the threshold limit value is its proper interpretation. Properly interpreted, these benchmarks are invaluable to the industrial hygienist. Careless interpretation can lead to confusion and faulty conclusions.

The careful selection of threshold limit information and its proper interpretation is an extremely important and vitally necessary task. It can be accomplished only by intensive research, careful recording and publication of pertinent information and by active participation and cooperation of all industrial hygiene interests. The establishment of reliable threshold limit values depends entirely upon such cooperation.

Permissible Dustiness

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SYSTEMATIC studies of health hazards in the dusty trades have demonstrated a direct relationship between: (a) the magnitude and duration of dust exposure and (b) the incidence and rate of production of dust disease. For separate industries, the findings have indicated that tolerable dust concentrations exist, below which disabling dust disease does not develop (in the absence of tuberculosis) over a normal span of working life. At such levels of dustiness the probability of silicosis developing, even in its earliest and non-disabling stage, is low. The maximum permissible concentrations which have been recommended for various industries are summarized in Table I.

Since silicosis is produced by the unique action of finely divided particles of free silica in the lungs, it has been generally assumed that the dust hazard varies in proportion to the quantity of this substance in the dust rather than in relation to the total dust concentration. From this assumption was derived the following rule, first proposed by Cummings¹¹ as a general guide in the development of dust control measures and later formulated as a more comprehensive expression of permissible dustiness:³ "Multiply the percentage of free silica by the total particle dust count. If the result is under five million, the condition may be considered permissible. If the result is over five million, the condition may be considered too high. For example, 10% free silica with an average total dust concentration of 30 million particles per cubic foot would give 0.1 times 30 million, which equals three million (good practice); 30% with an average total dust concentration of 50 million would equal 0.3 times 50 or 15 million (unsatisfactory). This formula is not applicable to any dust containing less than 5% free silica."

In proposing this rule, the Medical Committee of the National Silicosis Conference recognized its arbitrary nature but they

TABLE I.
RECOMMENDED LEVELS OF PERMISSIBLE DUSTINESS FOR VARIOUS INDUSTRIES

Industry	Percentage In Parent Material	Free Silica In Airborne Dust #	Recommended Level, mppcf	Sampling Instrument	Reference
Sydney Sandstone	90	7	6	Owens Counter	1
Silica Brick		75-90*	2	G-S Impinger	2
South Africa Gold Mines	80	2-5 μ :34† < 2 μ :23	3	Konimeter	3
Granite	26	32-39	9-20	G-S Impinger	4
Pottery	11-39	< 5 μ :12-37†	4	G-S Impinger	5
Gold Mining (Ontario)	25-35		8.5	Konimeter	3
Pyrophyllite		25-49	10	G-S Impinger	6
Non-ferrous mines		19-41	5-10	G-S Impinger	7
Anthracite Coal	< 6		50	G-S Impinger	8

*High content of cristobalite and tridymite in burned brick.

†Total Airborne dust, without reference to size, unless otherwise noted. The composition of dust commonly varies with size (9) and analysis should be on respirable fractions of airborne dust (10).

were also aware of the need for a practical guide in silicosis prevention, commensurate with good engineering practice and the best medical judgment. It was offered as an interim guide pending the accumulation of more comprehensive data from continuing studies of hazard versus exposure in actual industrial experience.

Dust Standards

THE RECOMMENDED levels of permissible dustiness are not to be taken as points of sharp cut-off below which no cases of silicosis can occur. In recognition of individual differences in susceptibility and because of the inherent errors in the assessment of individual exposures and in diagnosis of silicosis in its early stages, the findings have to be viewed statistically. The recommended standards must be regarded simply as giving a high probability that silicosis will not develop among exposed workers over a normal span of working life. It is clear from this that the validity of conclusions from any study is limited by the size of the exposed population in the study and the number of years of exposure.

In recognition of the statistical nature of the problem, Roach¹² has suggested that the dust hazard should be analyzed in terms of an exposure-response curve comparable to the dosage-response relationship employed in toxicological research.

In this way, the experience of the total exposed group in respect to development of the disease is used to estimate the dust tolerance level. This is in contrast to the dependence upon a small fraction of the total group, when the permissible level is fixed by noting the highest level of exposure

which fails to produce the disease. Such failure to find the disease is of limited significance when the population group is small.

According to the dose-response concept, some hazard exists with any level of dust exposure and the permissible level of dustiness is defined as that concentration below which the probable number of cases of pneumoconiosis will be kept within acceptable limits. The permitted level depends, of course, upon the seriousness of the disease and upon how early in its development it can be detected. Roach visualized a normal probability response curve, as in Fig. 1, where the logarithm of the total dose of dust (concentrations \times years of exposure) is plotted against percentage of individuals with silicosis in the several categories of exposure.

The position of the response curve along

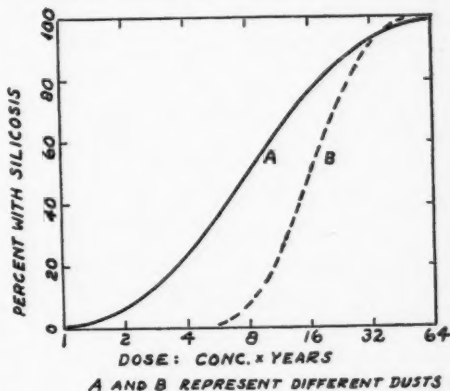


Fig. 1.
Log-normal dose-response curves.

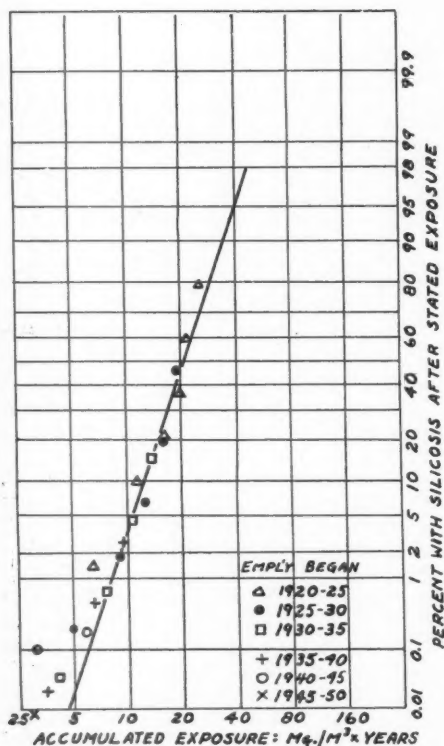


Fig. 2.

Development of silicosis in relation to total dust dose for successive "generations" of underground workers in South African gold mines.

the concentrations \times time axis indicates the relative damaging capacity of the dust and the slope of the curve is a measure of the variability in the relationship between dose and response caused by such factors as differences in individual susceptibility, errors in estimating exposure, etc.

Such an exposure-response curve, plotted on log-probability paper, is shown in Fig. 2 for the South African gold miners, the data coming from the Report of the Silicosis Medical Bureau for the year ending March 31, 1951.¹³ This plot, based upon yearly examinations of 25-30,000 individuals, shows the progressive development of silicosis in several "generations" of underground workers whose periods of employment began at various times prior to 1950 back to 1920, as indicated in the figure. Among men whose

employment started in 1920-25, 20% had developed silicosis after 15 years and by 1950 (30 years exposure) 80% of this generation had the disease. In the group who began work in 1935, on the other hand, only 2.3% had developed the disease after 15 years exposure. It is to be noted, however, that the different experiences of the several generations in respect to the development of silicosis fall on the same line, when the dust "dose" is expressed as the product of concentration and years of exposure. Dust concentration (mgms/m³) data were taken from Chamber of Mines reports^{14,15} and represent the average levels throughout the mines, as follows:

1920-25	1925-30	1930-35
1.3	1.0	0.8
1935-40	1940-45	1945-50
0.7	0.6	0.6 (est.)

There is remarkable conformance in Fig. 2 with the logarithmic dosage-response relationship found in other areas of toxicology and it thus supports the analytical procedure suggested by Roach for establishing levels of permissible dustiness.

According to the fitted line, one case of first-stage silicosis would be expected in a group of 100 men whose accumulated dust exposure amounted to (8 mgms/m³) \times years. To keep within this limit over a work span of, say, 30 years would require that the dust concentration be maintained below 0.27 mgms/m³. This may be compared with actual experience during the 15 year period 1935-50 when the average dust concentration was 0.6 mgms/m³. At the end of this period, 2.3 cases of early silicosis had developed per 100 initial employees.*

No distinction is made in this analysis between the drill runners and other underground workers (such as the ones at the ore passes) and it is assumed that the average dust concentration in the mines represents all exposures. The 1951 report of the Silicosis Medical Bureau (*loc cit*) includes a further breakdown of workers according

*At probability levels below 1/100, the number of cases of silicosis exceeds the number predicted from the log-probability line in Fig. 2. Three possible reasons for this are suggested: (1) There may be a certain probability of misdiagnosis of lung abnormalities not related, in fact, to dust exposure; (2) the excess cases may reflect hypersensitivity to dust in a few individuals; (3) these cases may represent dust exposures, in fact, above the average mine dust concentrations.

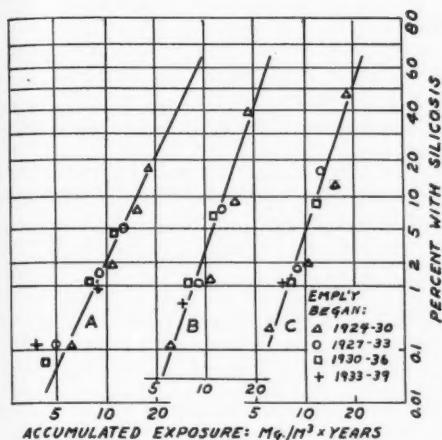


Fig. 3.

Development of silicosis in South African gold mines, in relation to total dose for successive "generations" of workers in three separate occupation groups: (1) no drilling experience; (2) < 50% time on drills; and (3) 50-100% time on drills.

to occupational history into four categories: (1) no work with drills; (2) up to 50% time on drills; (3) 50-100% time on drills; (4) drilling only.

From yearly silicosis production rates given for these separate categories one can construct dose-response curves as in Fig. 2, for successive generations in the several occupational groups. The results are shown in Fig. 3 for all except the fourth category (drilling only) which contained too few men for analysis. These plots show straight line dose-response relationships on log-probability paper, as do the data for the whole population. For categories 2 and 3 (up to 50% and the 50-100% time on drills), the lines are parallel with, and may be superimposed on, the line in Fig. 2 for the entire underground population.* Men with < 50% time on drills enjoyed a slight advantage over those who worked 50-100% of the time with drills; thus, after 18 to 24 years exposure, 39% had silicosis as compared with 48% of the men with histories of 50-100% time on drills.

*The majority of men in the total group with the longer years of exposure falls in categories 2 and 3. This explains the parallelism between the dose-response line for the total group and the line for the men with drilling experience.

With no drilling experience, the onset of silicosis was slower, requiring an estimated total of 33 mgms/m³ x years to produce the disease in 50% of the population as compared with 20 mgms/m³ x years for 50% silicosis in the group who spent 50-100% of their time operating drills. It is of interest to note, however, that the difference is chiefly in the slowness of development of the disease in the population (slope of line) and that about the same dose is required to produce silicosis at the probability level of one per 100 in all three groups.

In the absence of more detailed knowledge respecting dust concentrations and occupational histories for this large group of underground workers, it is not proper to draw any quantitative conclusions from this analysis of the South African data. The results are given simply to demonstrate the usefulness of the analytical procedure and to show the value of continuous collection of data on the production of silicosis among exposed workers in the dusty trades to give a firm basis for the establishment of permissible levels of dustiness.

No information is available on silicosis production in American industries comparable to the South African data. It is of interest, however, to examine in the foregoing manner the findings from the several cross-sectional studies of the dusty trades conducted by the U.S. Public Health Service.^{4,5,7,8} Exposure-response plots are shown in Fig. 4 for four exposed groups: granite cutters, pottery workers, non-ferrous metal miners, and anthracite coal miners. Straight lines have been fitted to the scattered points on the log-probability grid. From these lines, the following exposures are predicted as the maximum permissible levels to keep the probability of silicosis (first-stage) development to one case per 100 exposed workers:

Industry	Total particle-years	Maximum Conc. for 30 years exposure
Granite	40 x 10 ⁶	1.3 mppcf
Pottery	65 x 10 ⁶	2.2 mppcf
Metal Mines (non-ferrous)	100 x 10 ⁶	3.3 mppcf
Anthracite Coal mines	900 x 10 ⁶	30.0 mppcf

These figures may be compared with the previously recommended levels of dustiness

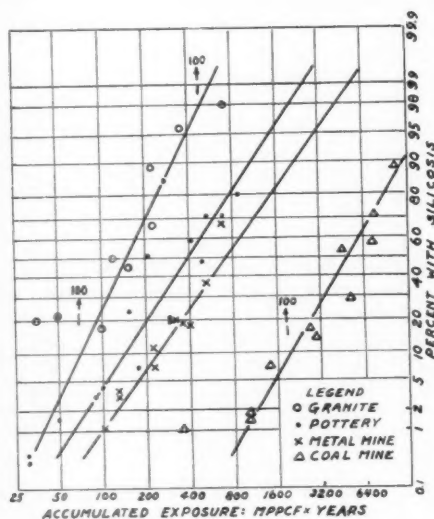


Fig. 4.

Development of silicosis in relation to total dust dose for workers in four separate (American) industries: granite cutting, potteries, non-ferrous metal mining, hard-coal mining.

for the respective industries: granite—9 to 20 mppcf; pottery—4 mppcf; non-ferrous metal mines—5 to 10 mppcf; anthracite mines—50 mppcf. There is a general lowering of the estimated levels of tolerance resulting from the new analysis but it must be pointed out that the considerable scatter of points in Fig. 4 limits the statistical significance of the exposure-response lines, as drawn. The most remarkable difference is in the figure for the granite industry which is based on the production of simple silicosis (to conform with the other studies) whereas in the PHS study, the level of 9-20 mppcf was recommended to prevent silico-tuberculosis. The development of this more advanced stage of the disease obviously requires a higher total dust dose. It is of interest to compare these figures with the equivalent weight concentrations. Assuming the mass average particle size to be two microns, there will be about 100×10^6 particles per milligram. Thus, the equivalent weight concentrations will be: granite = 0.48 mgms/m^3 ; pottery = 0.76 mgms/m^3 ; metal mines = 1.15 mgms/m^3 . These are of the order of concentrations reported for the South African gold mines.

Hazards

RETURNING, now, to the recommended levels of permissible dustiness in Table I, one sees little evidence of a correlation between the percentage of free silica in the parent material or the airborne dust and the silicosis hazard.* On the contrary, the proposed safe dust concentrations appear to be about the same for all exposures which produce a clear-cut silicosis hazard. Undoubtedly, a primary correlation does exist between the *effective dose* of free silica dust in the lungs and the consequent hazard but modifying factors peculiar to the industry and normal variability in individual response to dust tend to hide it. In each of the USPHS studies of the dusty trades, the point is made that the results of the study apply only to the industry in question and should not be generalized to cover other industries. In the face of this evidence, it would be well, perhaps, to abandon the general rule relating hazard to percentage of free silica and to consider the dusty trades in the following categories: (1) Industries in which a well-defined silicosis hazard exists—recommended level < 5 mppcf. (2) Industries in which the silicosis hazard is borderline—5-10 mppcf. (3) Industries in which the dust produces simple pneumoconiosis (coal mining, ? others)—25-50 mppcf. (4) Nuisance dusts (no demonstrable disease produced)— < 100 mppcf.

This proposal requires an adequate medical classification of the dusty trades and statistical demonstration of the way in which the production of dust disease varies with magnitude and years of exposure. It requires a further demonstration of the differences in hazard which may exist within an industry, as in foundries, for example, where the hazard apparently differs markedly between the molding floor and the cleaning room. It must give proper recognition to factors in the dust exposure which may modify the hazard, such as: particle size, degree of aggregation in the dust, presence of substances which lower the

*Recommended levels of 5-10 and 10-15 mppcf for exposure in hard rock (30% SiO_2) and haulageways (13% SiO_2) in anthracite mines³ are often pointed to in support of a correlation between dust hazard and free silica content of dust. These levels were not derived from actual experience in coal mines, however, but were simply estimated from experience in the granite industry and applied to the hard-coal mines.

toxic activity of silica¹⁶ or which produce pseudo-silicotic changes in chest x-rays.¹⁷

Fundamental to the success of occupational disease prevention is the concept of tolerance concentrations of toxic substances encountered in industry and the continued demonstration of useful correlations between nature and magnitude of exposure, as measured by industrial hygiene techniques, and nature and magnitude of response as measured by medical and epidemiological techniques. Outstanding contributions in support of these concepts have come from the systematic studies of the dusty trades, carried out in accordance with the procedures largely developed by the U.S. Public Health Service. The progress that has been made toward the elimination of silicosis from American industry stems in considerable measure from such studies. It is a matter of great concern, however, that one cannot determine exactly how much progress has been made because of the lack of published data. As the magnitude of hazard is lowered through dust control the need for more refinement in the determination of the levels of permissible dustiness increases. Continued teamwork between industrial physicians, hygienists, epidemiologists and others is required to complete the work on prevention of dust diseases in which so much has been accomplished to date.

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Gases

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TO DETERMINE whether the gaseous substances included in the current Threshold Limits List possess any distinctive or even unique characteristics that should direct our thinking when developing limits for their tolerated concentration in the working environment, it may be advisable to group them according to their generally-accepted primary physiologic action. Such an arrangement is reflected in Table I.

It may be noted that numerically the true gases comprise but a minor part of the list of gases and vapors. They constitute only 21 of 127 substances listed, or 1 in 6. Also, of these 21, more than half are general tissue irritants. With the exception of ammonia, which rarely reaches the lungs in high concentrations, they act as pulmonary irritants. Inhalation of these irritants in sufficient concentrations may cause pulmonary edema or even hemorrhage. This is

THRESHOLD LIMITS OF GASES
ACCORDING TO PRIMARY PHYSIOLOGIC EFFECTS

IRRITANT	Limit	ASPHYXIANT	Limit
	ppm		ppm
1. Ammonia	100	1. Carbon dioxide	5,000
2. Chlorine	1	2. Carbon monoxide	100
3. Fluorine	0.1	3. Cyclopropane*	400
4. Formaldehyde	5	4. Dichlorodifluoro-	
5. Hydrogen chloride	5	methane	1,000
6. Hydrogen fluoride	3	5. Dichloromethane	500
7. Nitrogen dioxide	5	6. Hydrogen cyanide	10
8. Ozone	0.1	SYSTEMIC	
9. Phosgene	1	1. Arsenic	0.05
10. Phosphine	0.05	2. Hydrogen selenide	0.05
11. Sulfur dioxide	10	3. Hydrogen sulfide	20
		4. Stibine	0.1

*More recently classified as a depressant of the central nervous system.

the most important consideration in setting threshold limit values for these substances because pulmonary injury developed from such sources is likely to be an "all-or-none" affair. There are no known antidotes or types of medical treatment that can be depended upon to reverse fully developed and severe pulmonary edema. This not only demands extreme caution in setting threshold values for such gases to assure prevention of such an effect, but also suggests the desirability of adding a second limit designed to protect against severe effects from short but intense exposures.

The irritant gases as well as some that are not irritants may cause discomfort in other ways, such as by unpleasant odor (H_2S , PH_3), disagreeable taste (SO_2), headache (O_3), eye irritation (H_2S), and choking (NH_3 , Cl_2 , HF), and often this factor enters into setting the limits. Although the Threshold Limits Committee of the American Conference of Governmental Industrial Hygienists places major emphasis on health for selection of the proper limiting air concentration of an injurious agent, with the increasing emphasis in occupational health on the "total man," comfort has now become also a determinant in the selection of a threshold limit value. Thus, whereas a threshold limit value of 3-4 ppm for chlorine would be adequate to prevent impairment of workers' health, this value is reduced to 1 ppm in the interest of greater freedom from irritant effects.

Irritant gases possess still another distinctive characteristic—the great range of individual susceptibility to their effects, not necessarily to the more serious effects

but certainly in respect of real or imagined discomfort. For example, psychologic associations with odors, unwillingness and incapacity to withstand irritations, and apprehension of choking and suffocation may vary widely among individuals according to past experience. Although at present these factors may not materially influence the selection of permissible threshold limits, in time, as additional information becomes available, occupational health practices will undoubtedly take them into consideration.

The asphyxiants act more insidiously than do the irritants because they are non-irritant and possess either no odor (carbon monoxide) or a not unpleasant odor (cyclopropane, hydrogen cyanide). It may be noted, however, that the threshold limits for these substances as a group are the highest of the entire group of gases. The substances with the two lowest levels, HCN, CO, could be equally well classified as systemic reactors.

Systemically acting gases are among those with the lowest threshold limit values. Among this group are some of the more toxic substances known. For substances as toxic as these, threshold limits have been set for all practical purposes on the basis of acute exposure (AsH_3). The reason is that (1) a single brief exposure greatly in excess of these values may prove fatal, and (2) chronic poisoning from certain gases in this group is virtually unknown.

As to the adequacy of the threshold limit values for gases, recent experience indicates that the values for at least three substances—nitrogen oxides, ozone, and carbon dioxide—should be revised. No recent dissatisfaction has been expressed or experience reported which would indicate that the present limits of the other gases are inappropriate. Indeed, on the other hand, for the first time evidence has been obtained from long industrial experience which would indicate that the value of 3 ppm for hydrogen fluoride is unquestionably a safe one. Although this substance has been in use for many years, its value had been set on very tenuous grounds.

Good experimental evidence now available from the Army Chemical Corps¹ indicates that the past limit of 25 ppm for nitrogen oxides should be revised downward to 5 ppm. Moreover, with the trend toward in-

creased refinement in designation of toxic agents, it is felt that the inclusion of all oxides of nitrogen under the heading of nitrogen oxides does not serve the best purpose, and that separate values should be assigned each oxide that represents an occupational health hazard. Of all the nitrogen oxides, nitrogen dioxide currently appears to be of greatest concern not only from its wide exposure hazard but from its toxicity as well.² The new value of 5 ppm is now to be applied to nitrogen dioxide. Information is being accumulated on which to base the limit for others of this group of gases. Exposures to nitric oxide (NO), such as occur from copper dip-tanks, are being studied industrially. Nitrogen pentoxide (N_2O_5), the gas associated with ozone in arc welding, is currently being investigated experimentally in England⁴ and by the Occupational Health Field Headquarters, U.S. Public Health Service.⁵ The other oxides of nitrogen are presently of little industrial concern.

The threshold limit for ozone is based on little sound supportive evidence. Although the current level of 1 ppm undoubtedly is sufficiently low to safeguard the exposed worker from serious pulmonary disability, recent experience with this material indicates this level to be unsatisfactory from the standpoint of irritating effects. In 1950, moreover, the controversial question raised by Thorp³ that nitrogen oxides were mainly responsible for the toxicity of ozone demanded reinvestigation of the entire problem. A progress report on this reevaluation by the Occupational Health Field Headquarters was given at the annual meeting of the American Industrial Hygiene Association in Chicago, 1954.⁵ Results of this work, combined with a critical review of past literature and current industrial experience, indicated the desirability of lowering the threshold limit of ozone to 0.1 ppm by volume. No evidence was obtained for depreciating the toxicity of ozone because of the possible presence of nitrogen oxides as previously asserted. As well as we can judge, and we have made numerous studies of a variety of responses from a large range of concentrations of ozone both alone and in combination with irritant nitrogenous gases, nitrogen oxides do not significantly alter the toxicity predictable on the basis

of the ozone concentration in the mixtures usually encountered.

The level of carbon dioxide appears to us to be somewhat conservatively low if one is to accept the conclusions of Consolazio *et al.*,⁶ who have made an extended study of its physiologic effects in man. Exposure to carbon dioxide is becoming increasingly important because of the longer periods of submersion of submarines as a result of the use of atomic power. Carbon dioxide exposure is also of importance in the handling of dry ice. The work of Consolazio *et al.* shows that the present level of 0.5% CO_2 could be raised at least fivefold, to 2.5%, without effects other than a slightly increased respiration (from 15 to 20 rpm) for exposures up to 72 hours, provided that the oxygen content of the air was not greatly reduced, although oxygen contents of the air as low as 12% were not severely discomforting at these levels. Concentrations much higher than 5% CO_2 were not well tolerated by healthy young men. Data with respect to later submarine tests of longer duration, which we hope will soon be made available by the U.S. Naval Medical Research Laboratory, may offer new information on which to base a firm threshold limit for carbon dioxide.

Although these represent the only gases to which the author's attention has been called, there are possibly others which may profitably be reconsidered as to suitability of choice of level. The gaseous mercaptans, now of increasing importance in the oil industries, are in need of studies leading to justifiable threshold limits; only scant experimental information exists on any of these substances. It is expected that in the near future toxicity studies on certain of these mercaptans will be reported by Dr. Brieger of the Jefferson Medical College of Philadelphia.

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Metal Fumes

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IN REGARD to threshold limits for metal fumes this report consists mostly of negative information, but it is believed that in the absence of positive knowledge, it is at least helpful to know what concentration of fumes has *not* affected health.

It is not a profound statement to suggest that the norm of an ideal M.A.C. is determined by the absence of specific occupational disease. This is not always practical since to insure this, one could set all M.A.C.'s at zero. If a limit is set too high, occupational disease will result; if pegged too low, it may be difficult to meet in practice and will soon be ignored. Ideally the standard should be such that even the most susceptible person can be exposed for a lifetime without experiencing occupational disease.

The safety people have concluded that all accidents, except those caused by acts of God are avoidable. However they have taken the position that it is impractical to prevent 2% of them and still operate industry. Could this also be true of occupational disease?

Atmospheric samples of exposures do not correctly measure industrial environment if an operation is not constant with respect to time and concentration of contamination. In this respect, M.A.C.'s are found wanting. For example, how does one by means of atmospheric samples determine the exposure of a lift truck operator who works in all departments of a plant and even outside the plant where exposures vary from area to area and from hour to hour. If one could use the exposed person himself as his own air sampler—much as is done by analyzing urine and blood specimens for lead—prior to any deleterious effects on him, one could then take into consideration all the variables of intermittency, fume floods, respiratory

rate, solubility, temperature, etc. For this reason biological M.A.C.'s are being considered and where applicable they probably would afford the best standard. This unfortunately cannot be used for all materials such as, for example, iron oxide.

Yant's excellent paper "Industrial Hygiene Codes and Regulations" reprinted from the 13th Annual Meeting of the Industrial Hygiene Foundation covers very well the major points that beset us with regard to M.A.C.'s.

The M.A.C. is not a value that should be maintained or permitted to exist just because it may be tolerated. If practical, industrial exposures should be reduced even below the so-called hygienic standard.

In regard to specific metallic fumes, we have had experience with the following: Beryllium, Chromium, Iron oxide, Lead, Manganese, Tellurium, Zinc.

We have processed beryllium copper castings for about two years. The approximate analysis of our heats is as follows:

Tin	trace
Aluminum	0.01%
Iron	0.07%
Lead	0.10%
Zinc	0.13%
Beryllium	0.18%
Nickel	1.50%
Copper	97.99%

The fume evolved, as far as beryllium is concerned, is the oxide, and the concentrations have ranged from 0.02 to 0.39 micrograms per cubic meter of air with an average of 0.18 micrograms.

With this degree of atmospheric concentration and duration of exposure, we can say that to date, no signs or symptoms of berylliosis have appeared. Of itself this information is of little value but if a sufficient number of experiences with beryllium fume is reported it will be possible to collate them and use them as a basis for suggesting an M.A.C.

Chromium as such, except for the chromates, dichromates, and chromic acid, has not been considered a significant industrial hazard. However we have had complaints from workmen in three different plants involving the burning and grinding of high chrome steels, stainless steel, and chrome molybdenum steel.

These complaints were hardly imaginary since when steels containing no chromium

were substituted, criticism ceased. The complaints occurred when the concentration of chromium, expressed as chromium trioxide (CrO_3), exceeded 0.2 milligram per cubic meter of air. There were no chromates or dichromates in the fume as shown by the diphenyl carbazide test. It is probably Cr_2O_3 .

While these data are not conclusive evidence, they are suggestive that the M.A.C. for chromium may not be exceeded.

Iron oxide fume produces the well known chest condition called siderosis. In a study made by us and which was published in *Industrial Medicine* in 1950, we showed that cases of siderosis developed in a short period of time with exposures that ranged from 19 to 90 milligrams of iron per cubic meter of air—the average was 39 milligrams. We are beginning since that time to find new cases occurring with exposures in the region of 15 milligrams per cubic meter of air.

Based on our experience, we do not believe concentration of iron oxide fume can greatly exceed 10 milligrams per cubic meter without eventually producing cases. We have adopted our own M.A.C. of five milligrams per cubic meter of air.

Lead and its compounds are important materials in industry. The fumes from melting lead are in the form of the oxide. From our experience with thousands of air, blood, and urine samples we believe that the present M.A.C. of 0.15 milligrams per cubic meter is safe for even susceptible persons in our plants.

We did not find cases of lead poisoning with continued exposures to concentrations of 0.3 milligrams per cubic meter. We did experience cases after a five year exposure

to concentrations of 0.5 milligrams per cubic meter. It should be borne in mind that this refers to the oxide.

The suggested M.A.C. for manganese is six milligrams per cubic meter of air. In our plants the concentrations of manganese have never exceeded this value and we have never had any cases of manganese poisoning from the fumes of this metal.

It appears from our experience at least, that this standard is satisfactory.

If one considers tellurium as a metal it comes under the subject assigned here. The M.A.C. for this material has been suggested as 0.1 milligram per cubic meter of air. For ten years now we have kept exposures below the M.A.C. and we have found no signs or symptoms of tellurium poisoning. Prior to control measures, however, when atmospheric concentrations were in the region of 0.3 milligram per cubic meter a definite garlic odor was noted on all exposed personnel but there were no more serious effects than that. In order to avoid the garlic odor, the M.A.C. for tellurium should not be increased.

Our exposures to zinc fume are slight. In a period of 12 years we have never found a case of metal fume fever. Our atmospheric concentrations ranged from 0.2 to 4.1 milligrams per cubic meter of air (av. 0.85). These values are far below the suggested limit of 15 milligrams per cubic meter of air.

Experience with the metals here considered leads us to believe that the M.A.C.: for lead oxide may be increased; for iron oxide should be decreased; and for the other fumes mentioned, be retained until there are sufficient data to warrant change.

Human Maintenance in Industry

THE 1955 Symposium on Human Maintenance, "The Handling and Control of Industrial Solvents," will be held at the Case Institute of Technology, 10900 Euclid Avenue, Cleveland 6, Ohio, on March 16, 17 and 18. The subject of Solvent Control was chosen for this program since it presents a potential hazard common to practically every industry. The purpose of the Symposium is to provide a practical knowledge of the hazards involved in using solvents, to provide information to enable industrial management to evaluate that hazard, and to outline practical and economical methods of control.

The Industrial Hygienist and Ear Protection

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THE INDUSTRIAL hygienist is regularly called upon to deal with atmospheric contaminants, of which industrial noise is one. It is unfortunately true at the present time that maximum allowable exposures to this agent are not known with certainty. To some extent, the hygienist has at his disposal techniques similar to those which he would use in related problems, such as handling of dust, gases, and vapors. When necessary, the hygienist is prepared to use personal protective equipment. Ear protectors belong in such a category.¹ The hygienist ought to know about their properties; he ought also to know about the interaction between protectors and the men who must wear them. The following discussion deals with these factors.

Principles of Ear Protection

THE OBJECT of ear protection is to reduce the level of the offending noise at the inner ear in order to prevent damage which results in a noticeable hearing loss. Naturally, the more reduction at the inner ear that can be obtained, the less danger there is to this structure. However, there are certain limitations which make it impossible to arrive at complete protection. Some of these limits are well understood, but others are still a considerable mystery.

For example: the mechanism of hearing is divided into two sections. One, that part which conducts sound via air, and two, by way of the nerve structure of the ear.* When the sound pressure becomes high

enough, the sound waves are conducted to the inner ear via the skull, and the air conduction part of the mechanism begins to be by-passed. Fortunately, there is a differential between the two mechanisms of about 50 decibels. In other words, unless the sound pressure is 50 db. or more, re: normal hearing, all the stimulus arrives at the inner ear via the air conduction system. As the sound pressure increases above this level, however, sound begins to travel to the inner ear via the bones of the skull. This places a limit on the available protection via the external auditory canal.

With this in mind one would immediately think of a helmet or over-the-ear protector included in a helmet. However, the same limitation applies here since the sound waves are carried to the skull via the chest cavity, the abdominal cavity, the skeletal bones and the bones of the face.

The effects of this limitation are well demonstrated in cases where a congenital defect has produced a complete absence of the external ear canal and sometimes even the middle ear. In cases such as these, audiometry will show as much as a 50 or 55 db. difference between air and bone conduction in the frequencies between 250 cps. and 8000 cps.

One would assume from this that insert type ear protectors should produce similar results. Unfortunately, this is not the case. The best of the insert type ear protectors produce only 20 to 25 db. of loss in the frequencies below 1000 cycles. This is considerably better than that which is found in the muff type ear protector which

* (1) The external and middle ear, and (2) the inner ear and auditory nerve.

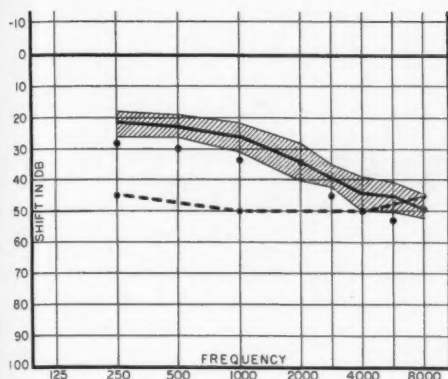


Fig. 1.

Shaded area shows median losses and interquartile range of the insert. Black dots show calculated maximum loss.⁵ Dashed line shows loss measured on congenital ear.

also produces losses above 1000 cycles of as much as 35 to 45 db. or even more in some cases, but considerably less below 1000 cycles. There is a noticeable difference then between the theoretical and practical limits. The causes of this discrepancy are not well understood and furthermore, have no place in this particular discussion.

Variability in Amount of Protection

THE CURVES shown in Fig. 1 indicate the differences between the calculated limits,² the limits obtained by congenital absence of the external and middle ear and those produced by the better of the insert type ear plugs.

It must be understood, however, that the latter curve is based on standard testing conditions as well as careful fitting of the ear insert, which brings us to one of the most common causes of reduction of efficiency, i.e., variability in the seal between the ear insert and the surface of the external auditory canal. Because of the discomfort produced by any tight-fitting object in the external auditory canal, the worker is dissuaded from obtaining a good seal. Conversely if there is no sensation of pressure in the external auditory canal there is inadequate protection. Further, the amount of discomfort produced by a well fitted ear protector is more psychological than actual in most people, and eventually

the wearer will become unaware of this discomfort. It should be remembered, however, that discomfort is probably the most frequent cause of variability in the efficiency of the insert type ear protector.

The materials that are used to fabricate ear protectors have a definite effect on their variability, not so much because the consistency of the material effects the transmission loss, but related to the ability of the material to conform to the shape of the external auditory canal from individual to individual or even between the two ears in the same individual. The materials must allow for changes in the external canal produced by motions of the temporo-mandibular joint and the auricle. Some of the variability produced by minor differences in size between the ear protector and external auditory canal may be eliminated by the use of lubrication. Fig. 2 will demonstrate this effect.

Testing Ear Protectors*

AT THE PRESENT time there is no standard method for testing the performance of ear protectors of any kind. The American Standards Association is well aware of this lack and has appointed a committee to make recommendations regarding a standard procedure for testing these types of appliances. In the meantime, however, it has been generally accepted that the following procedure is the best way to determine the efficiency of

*A forthcoming paper will discuss this more fully.

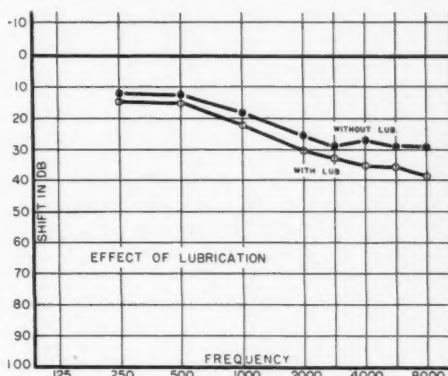


Fig. 2.

Average increase in loss when lubrication is applied to several types of inserts.

any type of ear protector now available. The principle of the method is based on the shift in threshold between the unoccluded and the occluded ear. However, because of the effect of earphones on insert type ear protectors and the impossibility of applying an earphone over a helmet or a muff type, the test is done in a free field. As is well known, such a test procedure has many limitations particularly where pure tones are used.

However, if one is careful to fix the head in a relatively stable position in a test room which is designed to have a low reverberation time, quite good results may be obtained since the difference is a relative one. Discrete frequencies are first introduced into the free field while the subject's ears are unoccluded and then again after the ear protectors have been fitted. Obviously, this is a binaural test, and the ear with the lesser attenuation is the one which is being tested. This may appear to be a weakness, but actually, the loss recorded is that of the least protection assuring an equal or greater loss in the opposite ear. Both graphs are the threshold curves for pure tones in the unoccluded and occluded ear, and the difference is due to transmission loss or the attenuation properties of the ear protector. It is not our purpose to discuss recommendations for testing in detail. The method is merely presented for the readers' information. As a general rule, industry does not test ear protectors, but it should know what can be expected of them in terms of an acceptable test.

Medical Aspects of Ear Protection

BEFORE an effective hearing conservation program is initiated it is well to understand a few of the medical aspects of ear protection and what some of the possible complications may be.

EXTERNAL EAR: Like all other organisms the human is individualized in all respects where anatomical configurations are concerned. All of us know that there are no two sets of fingerprints that are alike in detail. This is also true of the ear. Casual inspection of the external ear shows very few gross differences among external canals. However, the differences that do exist are notable in that they have a direct bearing on the "fit" of the insert type ear protector.

These differences may be classified under size, direction of and configuration of the canal from the plane of the ostium to the drumhead.

SIZE OF THE EXTERNAL AUDITORY CANAL: Even random inspection will convince anyone that the ear canal has wide variations in size. In general these measurements vary between 8-12 mm. in diameter and about 24 mm. in length measured from the external ostium to the drumhead.

Cunningham³ gives the following figures for the various diameters encountered in the external auditory canal. Starting at the plane of the ostium the diameter varies between the largest at 9.08 mm. to the smallest or 6.54 mm. At a plane about 8 mm. from the ostium the diameter measures 7.79 mm. for the largest and 5.99 mm. for the smallest. A more medial plane, about 10-12 mm. from the ostium, varies between 8.67 and 6.07, while at the drumhead the measurements vary between 8.13 and 4.60 mm.

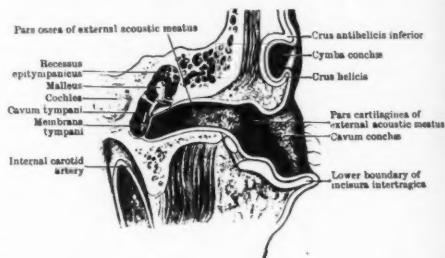


Fig. 3.
Frontal section of external auditory canal. Reprinted from Cunningham's Textbook of Anatomy.³

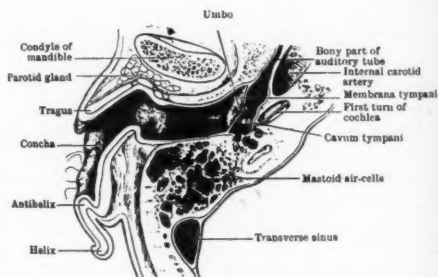


Fig. 4.
Horizontal section of external auditory canal. Reprinted from Cunningham's Textbook of Anatomy.³

Cunningham gives the length of the external auditory canal as about 24 mm. when measured from the most medial or deepest part of the concha or pinna to the drumhead.

A search of the literature adds little to these measurements. If, however, we are to judge the variations in size by the requests for insert type ear protectors, we are forced to conclude that the diameter of the outer third of the external auditory canal varies between 5 and 13 mm. It is highly probable, however, that the large majority will measure between 8 and 11 mm.

Perhaps another important variable to be considered is the position of the tragus (the small projection in front of the canal) in relation to the canal opening. Many times this projection extends too far backwards over the canal opening and prevents the insertion of the ear protector to its full depth. It may also exert pressure on the protector, forcing it backward and outward, and displacing it enough to produce an acoustic leak.

SHAPE OF THE EXTERNAL AUDITORY CANAL:

One of the most important measurements which influences the wearability of ear protectors is the distance from the ostium to the start of the first bend. Fitting ear protectors would be much less difficult if the canal were straight throughout its entire length.

Variations in direction would not be too troublesome provided the canal were straight, but in the human ear we are not only concerned with variations in direction but also variations in configurations and the direction the configurations take over the entire length of the canal. It is highly probable that most of the discomfort complained of is due more to the bends in the canal than to the discrepancies between protector and canal diameter-wise. The external third of the canal is rather pliable because of its cartilaginous and subcutaneous structure. The cartilaginous portion does not form a complete circle but a "U" shape where the ends of the U are joined by a fibrous band at the top. This allows for considerable pliability in the diameter and therefore considerable latitude in the ear protector diameter, provided the ear protector does not reach the first bend in the canal. The canal varies in diameter size

in different planes, but in general it grows smaller as it extends inward or medially. In other words, the external auditory canal is, in general, funnel shaped with the small end pointed medially or inward. This is especially true of the outer one third and therefore important since most ear protectors do not extend beyond this point and in many cases are gradually displaced outward because of the decreased diameter medially, resulting in acoustic leaks.

This discussion would not be complete if we did not include the effect of movement of the lower jaw on the external canal. All of us move our lower jaw many times during the day when talking, chewing, yawning, or swallowing; and consequently change the diameter of the outer third of the external auditory canal, some more than others. In any case such movements tend to displace even a well-fitted ear protector, and if the wearer is not aware of this, the protection afforded can be reduced considerably.

NON-STRUCTURAL FACTORS: Now let us discuss those factors which are not directly related to the anatomical structure of the ear. The skin of the outer $\frac{1}{3}$ of the external auditory canal contains glands that secrete cerumen or wax. All ears secrete some wax, and the average amount does not tend to accumulate in the auditory canal. It is moved outward by the motions of the jaw, gravity, and the hair growing in the canal. However, when the amount secreted is more than can be extruded, the wax will accumulate and serve to obstruct the insertion of the ear protector, resulting in a poor seal. On the other hand, the ear protector may push the wax inward toward the drumhead and cause further discomfort. In these cases it is important to have a physician remove the wax at regular intervals.

Perspiration should cause no real difficulty if the ear protectors are removed occasionally by those workers who perspire very freely or work in excessive heat.

Exostoses or bony projections from the bony part of the auditory canal are found in quite a few individuals. Unless these are large they should offer no obstruction to an ear protector since it rarely projects beyond the outer $\frac{1}{3}$ of the canal.

Existing external otitis or infection of the skin and subcutaneous tissue of the canal is a direct contra-indication to wear-

ing ear protectors. This is a very troublesome disease and offers a great deal of resistance to treatment under the best of conditions. On the other hand, cases of external otitis resulting directly from wearing ear protectors are exceedingly rare provided the material in the ear protector is an inert non-toxic substance similar to neoprene, polyvinyl plastic, or rubber. Those few cases reported are more often due to failure to keep the ear protectors reasonably clean. This applies to boils in the ear canal also.

There are over one million hearing aid wearers in this country who use inserts in the external auditory canal. These inserts are made from various substances similar to that used in fabricating ear protectors. Most hearing aid users wear the inserts from 12 to 16 hours a day. In spite of this, external otitis is quite rare among these individuals. This experience alone should serve to allay any fears regarding external otitis due to wearing ear protectors. Dr. Clarence Lloyd of North American Aviation, Dr. C. I. Barron of Lockheed Aircraft, and Dr. Thrift G. Hanks of Boeing Airplane Company, have repeatedly examined thousands of workers who had worn ear protectors for several years and all emphatically deny the existence of external otitis due to wearing ear protectors.⁴

Industry, no doubt, employs a considerable number of workers who have middle ear disease with accompanying discharge. Unless this discharge is a free running frank, purulent discharge, wearing ear protectors will probably have no adverse effects on the condition if the normal amount of medical care is provided.

Ventilation of the canal is not important enough under ordinary industrial conditions to provide for a constant exchange of air behind the protector. Sudden altitude changes which aviators encounter are another matter. These are specialized cases and special provisions should be made to counteract results brought about by a tightly closed system.⁵

Causes of Discomfort

EXCESSIVE pressure over any cartilage causes ischemia of the skin and subcutaneous tissues which results in pain. Most presently designed ear protectors exert pressure on the cartilaginous portion of

the external auditory canal. We feel that an adequate seal is obtained without excessive pressure and that when an adequate seal is obtained, further pressure is unnecessary. As previously stated, discomfort is more likely to be due to the pressure exerted on the first bend in the canal by the distal end of the protector. If the protector is long and no provision is made to conform to the change in direction, undue discomfort is the result.

Some ear protectors are fabricated with a ridge on the surface. This is probably due to the design of the mold used by the manufacturer. Such ridges will cause severe discomfort because of the small pressure area produced and should be avoided in all cases. The problem of discomfort is not a simple structural one. No one will deny that safety glasses and safety shoes have passed through the same cycle.

There is no doubt that the discomfort first experienced from a well-fitted ear protector eventually is relatively non-existent. Most of the objections to ear protectors can be overcome by good employer relations and education. Like every other protective device the worker must be convinced of the worth of the ear protector.

Material in the Ear Protector

THERE ARE many materials used in the fabrication of ear protectors, ranging from milkweed floss to lead. Outside of the need for attenuation there are two important factors to consider when choosing a material for ear protectors. First, does it produce a toxic reaction when placed in contact with the skin? Second, is it stiff enough to injure the ear if struck? Most of the presently used materials are non-toxic but some ear protectors are hard enough to cause considerable damage to the auditory canal and sometimes the drumhead even from a relatively gentle blow over the ear.

Muff-Type Ear Protectors

NATURALLY, when one thinks of ear protection, the muff type protector must be considered. There are those who believe muffs are the real answer to ear protection. From a medical standpoint, we can see no particular advantage and there is one important disadvantage. It is true that muffs do not require putting anything into the

ear and are, therefore, said to be more comfortable which in turn makes them more acceptable. We believe that muffs produce considerably less loss than plugs at frequencies below 1000 and, therefore, are less effective ear protectors.* With such a disadvantage the questionable difference in comfort is unimportant. Consider for a moment this problem of less loss below 1000 cps. The difference is enough to cause considerable concern to the doctor, for our present thinking places some of the blame for noise induced hearing loss on the frequencies between 300 and 1200 cps.⁶ If this is true, is it not safe to assume that plugs are better than muffs even in the sound pressure levels that exist in the majority of industrial situations?

In our opinion the question of comfort is a relative matter. There are those who feel that ear muffs are as uncomfortable as ear plugs and that adaptation is necessary for both.

Muffs do have a definite place when used in combination with plugs to produce the maximum protection available against noise levels which are beyond those encountered in most industries. The production of skin irritations or discomfort by muffs is analogous to ear plugs. The materials must be non-toxic and inert. The pressure exerted on the auricle or pinna must not cause ischemia or pain will result. The fitting problem for muffs is not as critical as with plugs but it should not be neglected, otherwise, the headband may be displaced and produce discomfort or acoustic leaks around the ear, particularly adjacent to the mastoid tip and parotid gland area.

Responsibility for Fitting Ear Protectors

THE RESPONSIBILITY for fitting ear protectors should definitely be delegated to a medical man. It is not always possible for the doctor to do the actual fitting, but he should at least supervise the process and check the results. In the past and even at present, in most cases ear protectors are fabricated and distributed in pairs. This would appear on the surface to be the natural procedure since ears also come in pairs. However, when careful checks are

made of the plug type ear protectors while in the ear, it will be found that many individuals require a different size in each ear if a proper fit is to be assured. This fact has recently been allowed for in the Armed Forces by new ear protector specifications which call for single protectors of various sizes rather than pairs. These same specifications place the responsibility for distributing the ear protectors in the medical department of each of the services.⁷

It is apparent that industry would do well to follow this procedure wherever possible. Such a system will insure prefitting examinations and prevent aggravation of existing disease as well as poor fitting ear protectors.

Conclusions

1. Even though presently available ear protectors do not afford the maximum protection possible, they must be included in a hearing conservation program.

2. Insert type ear protectors afford more protection than muff types and are therefore the better choice.

3. Discomfort from insert type ear protectors is to be expected but most individuals adapt to it quite easily in a short time.

4. Lubricated insert type ear protectors afford a better seal and therefore more protection.

5. The present method of choice for testing the efficacy of ear protectors is a pure tone free field measurement of the threshold shift produced by the protector when fitted in the human ear.

6. External otitis (infection in the auditory canal) is rarely due to wearing insert type ear protectors.

7. The distribution and fitting of ear protectors should be under medical supervision.

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*This treatment is based on measurements made on many types of muffs by the authors in their own laboratory.

An Industrial Hygiene Program—

FOR A BENZENE EXTRACTION PLANT IN A PETROLEUM REFINERY

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Esso Standard Oil Company, Louisiana Division, Baton Rouge, Louisiana

THE RAPIDLY expanding production of a wide variety of chemicals from petroleum provides a new challenge to the industrial hygienist in evaluating and controlling potential industrial health problems.

Among petrochemicals produced at our refinery, benzene occupies a position of major importance. The following program was developed for the protection of the health of refinery employees against the acute and chronic types of poisoning from this product.

Toxicology of Benzene

THE TOXICOLOGY of benzene has been adequately described in the work of Flurry¹ on acute benzene poisoning, of Mallory *et al*² on chronic poisoning and of Greenburg *et al*³ on benzene poisoning in industry.

Benzene Plant

BENZENE is present in hydrocarbon streams produced in our petrochemical operations in concentrations ranging from nil through 99% purity. The Benzene Plant streams are primarily within the upper range of concentrations and every stream from feed stock to finished product contains amounts of benzene significant from the health standpoint.

The Protective Program

A. DESIGN STAGE:

Early realization of potential health problems involved in the operation of the Benzene Plant made possible the inclusion of protective measures in its design. Consultations with the engineering groups responsible for design and layout enabled the Medical Department to visualize the major problems which might arise. The consultations were also useful in educating the en-

gineers to the industrial health aspects of benzene exposures. With their cooperation, it was possible to include many protective features such as sealed drains to sewers, improved sampling station drains, venting of benzene-handling pumps to closed systems, and provision of double block valves and bleeders where necessary. A small laboratory where benzene samples would routinely be handled was isolated from the control room and provided with a laboratory type exhaust hood. Location of the control room was adequately removed from process equipment and tankage to insure that general ventilation of this building was sufficient protection against the build-up of benzene vapor concentrations.

B. EDUCATIONAL PROGRAM:

Believing that it would be desirable to educate the individual employee to the health problems of benzene, a series of meetings was arranged with the process and mechanical groups to be assigned to the unit during the start-up period and on a permanent basis.

In these talks, a portion of the program was devoted to each of three subjects; the Refinery Medical Director spoke on the medical aspects of benzene poisoning, the Industrial Hygienist spoke on the protective measures and the protective program, and a representative of the Safety Department spoke on the use of protective equipment. During each meeting, questions were solicited from the group and informal discussions were held.

C. EMERGENCY FIRST AID EQUIPMENT:

In view of the extreme rapidity of acute benzene poisoning under more severe conditions, special attention was paid to the provision of emergency first-aid equipment and supplies.

Although most of our employees are acquainted with the techniques of artificial respiration, it was believed desirable to have readily available an inhalator with spare cylinders of 93% to 7% mixture of oxygen and carbon dioxide.

D. PROTECTIVE EQUIPMENT:

For the most severe exposures to benzene vapors from spray or leaks, self-contained respirators were placed in the control room for use in emergencies such as shutting down the unit or rescue of personnel.

During the start-up period of the unit, it was felt desirable to have available some type of respiratory protection against relatively low concentrations of vapor. Although limited by low capacity and relatively low effectiveness, the chemical cartridge respirator is light and fairly comfortable to wear for extended periods. It is more acceptable to the employees, and will be worn more readily than the heavier type canister gas mask. Cartridges were changed daily or upon first detecting the odor of benzene through the cartridge.

The chemical cartridge respirator was not intended as a permanent solution for exposures to low, though unsafe, concentrations of benzene, but rather as a means of obtaining the fullest possible protection during the start-up period and immediately after. It is our policy to correct by engineering methods all conditions causing the air concentrations to exceed the threshold limit value of 35 parts per million of benzene by volume in air.⁴

E. AIR SAMPLES:

As soon as the production of benzene at the unit had begun, routine air samples were taken in strategic areas by personnel of the laboratory. Some five to seven tests were made daily in the designated areas, and in addition, tests were made any time the plant operator desired them.

At first, instruments available for the field analysis of benzene in air were limited to one general type, that of the heated filament-combustible gas indicator type calibrated for benzene. At about the time the unit started operation, however, there became commercially available a colorimetric ampule type instrument based on the method described by Hubbard and Silverman.⁵ This instrument was greatly preferred over the former type because of its smaller size,

increased sensitivity and, as was first thought, its specific detection of aromatics.

Although toluene might also be present to some extent in the atmosphere, it was decided to read the instrument as entirely benzene, since this latter material was of much greater importance volume per volume.

In calibrating the aromatic hydrocarbon detector in the laboratory, it was noticed that some other compounds gave stains which could be confused with those produced by benzene, toluene or xylene. Butadiene 1-3 reacted markedly, giving a dark stain very much like that of benzene. Isoprene and piperylene act much like benzene, except the stains are yellow at first and then darken to brown. Neither normal butane nor normal butenes produce a stain, but both of these compounds in high concentrations had the effect of preventing subsequent reaction with benzene. Because of this effect, any tubes which might possibly have come in contact with butane or butenes were discarded and not reused.

F. URINARY SULFATE RATIOS:

The value of the shift in the ratio of inorganic to total sulfates in the urine as an index of benzene absorption has been shown by the work of Schrenk⁶ and of Bowditch and Elkins.⁷ Although there appears to be limitations and some exceptions to this method of evaluating benzene absorption, it becomes all the more important as an adjunct to air analyses, plant studies and medical examinations.

Either of two analytical methods for determining the sulfate ratio may be employed. One is a simple gravimetric method suitable for concise determination of the amount of inorganic sulfate and the amount of total sulfate in the sample. The method preferred by our laboratory because of its adaptability to the analyses of large numbers of samples is the volumetric procedure of Hawk and Bergeim.⁸

During the first weeks of operation of the unit, urine samples were collected from each employee as frequently as once per week. Samples were collected at the end of each shift and were refrigerated when analyses could not be performed within two or three hours. Several complete group determinations revealed no excessive absorption of benzene. After plant conditions were stabil-

ized and a recheck of the group was completed, the frequency was lowered to once every two months.

At the present time, the mechanical and process groups are checked about every three months. The results of these analyses have been in agreement with atmospheric concentrations reported and with general operating conditions observed.

G. BLOOD STUDIES:

Employees tentatively assigned to the unit received special physical examinations designed to reveal any physical limitations; such as, kidney, blood or heart disease before being permanently assigned. Base line blood smears were made for comparison with ones to be made at 6 month intervals.

Engineering Improvement

A. GENERAL:

In the actual construction of the plant, all efforts were directed toward having a leak-tight, completely enclosed system throughout. Before the unit was placed into operation, a vacuum test showed the system to be in unusually tight condition. Little trouble with leaks and blow outs was experienced during the start-up of the unit and thereafter.

B. MECHANICAL SEALS:

The engineering change having the greatest effect of lowering benzene concentrations in air at the unit was that of substituting mechanical seals for ordinary packed glands in pumps handling benzene-rich streams. Atmospheric benzene concentrations, within the operating area of the unit, were unsatisfactorily high until the installation of mechanical seals on principal pumps in the vicinity reduced the levels to practically zero.

Maintenance engineers are sometimes reluctant to install mechanical seals throughout, since a failure of this type of seal cannot be repaired without shutting down the pump. The usual practice is to install mechanical seals on the regular pumps and leave pumps with ordinary packing as spares, as the latter type can be repaired during operation.

C. LOADING RACK:

The product benzene is shipped in railroad tank cars from a 10-station loading rack. The potential exposures at the load-

ing racks were considered to be of more significance than at most locations in the unit itself. Exposures arise from several different sources, namely:

1. Displacement of benzene vapor-laden air from the tank car through the dome during the loading operation.

2. Leakage from the tank car foot valve. The foot valve of a railroad tank car is controlled by a wheel mechanism on the dome of the car, and the valve is covered by a screw cap during actual transportation of the car. Foot valves are sometimes in poor condition causing leakage of the product to such an extent that the car must be rejected and returned to the tank car operating company for repair. However, excessive leakage may not become apparent until the car has been partially filled with benzene. Standard procedure is to attempt to reseal the foot valve by opening the valve suddenly to allow a surge of benzene to flush out any sediment which might be preventing the valve from seating properly. This flushing procedure may be tried several times before the decision is made to reject the car. The flushed benzene, amounting to several gallons for each attempt at flushing, together with the benzene which has been continuously leaking past the valve, must be collected and removed to prevent evaporation or ground absorption.

3. Leakage from the loading system during the times the system is under pumping pressure. This leakage usually occurs at the gate valves at the unoccupied loading stations. Ordinary gate valves, even those in good condition, cannot always completely shut off the seepage of benzene past the valve seat when loading pressure is applied to the loading line. The quick opening valve on the end of the swing pipe is also subject to leakage due to thermal expansion of trapped benzene between this valve and the gate valve.

The solution of these three engineering problems was the result of study by the engineering department, the loading rack supervisory personnel and the industrial hygienist.

The removal of the displaced vapors from tank car loading was accomplished by constructing a plastic dome cover which is bolted over the top of the dome (Fig. 1).

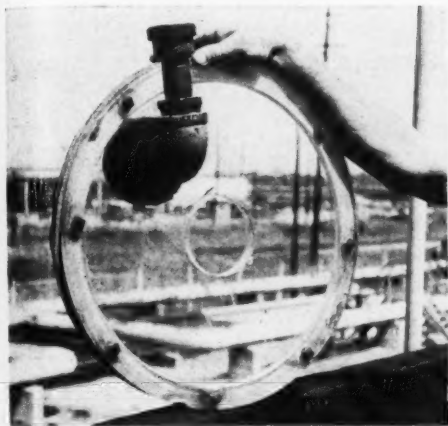


Fig. 1.

Clear plastic dome covers provide maximum visibility of tank car benzene levels.

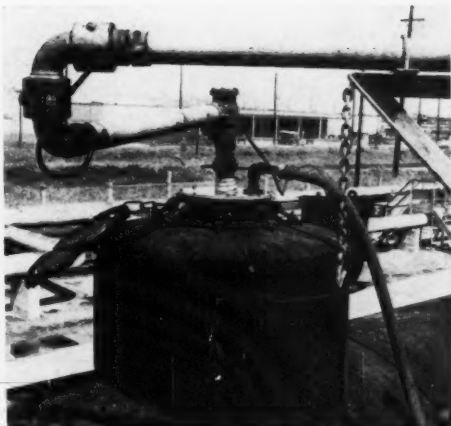


Fig. 2.

Dome cover in place with loading spout and vapor vent line connected.

Full plastic domes were used to allow maximum visibility of the benzene level in the tank car. The cover has a hole in the center through which the downspout is inserted to allow under-surface loading. A soft neoprene gasket is used to prevent leakage of vapors through the annular space between the cover and the downspout and another gasket around the periphery of the cover prevents escape of vapors from the space between the dome and the plastic cover (Fig. 2). Leading off from the dome cover is a flexible rubber hose connected to a manifold system with a central vent releasing the vapors at a point above the loading rack. Changes in plant design have allowed the vent system to be tied into a water eductor unit thereby providing a source of vacuum for more satisfactory removal of vapors from the dome.

The health problem resulting from foot valve leakage has been almost completely controlled by the installation of drainage pans spotted beneath the foot valves of the tank cars to catch the leakage and flushed benzene. The pans are tied into a sewer line leading into the benzene plant waste separator (Fig. 3).

Leakage past the gate valves were controlled by tapping the valve at a point just above the valve seat and attaching a 1" line leading to a manifold system beneath the rack. This small line is fitted with a



Fig. 3.

Pans beneath tank car foot valves drain spills and leaks to sewer.

valve which is left open at all times except when actually loading from that station. The manifold system drains into a small collecting tank and the recovered benzene is pumped into crude benzene storage for re-finishing (Fig. 4).

D. CONTINUOUSLY RECORDING BENZENE ALARM:

In order to afford an extra margin of safety from sudden leaks or breaks in the benzene lines, a combustible gas type instrument calibrated for benzene was installed at the unit. This instrument is merely an adaptation of the usual type of gas alarm system used in solvent extraction

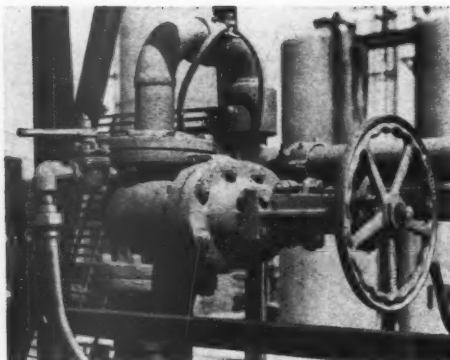


Fig. 4.
Leakage past gate valves is drained through small line into recovery system.

plants and other locations where explosive vapors are the primary hazard. The instrument continuously analyzes and records the results of samples drawn from eight sampling points located throughout the unit. An alarm is sounded when an air sample from a collection point contains over a certain percentage of the lower explosive limit of benzene. The instrument was designed to alarm at a 100% benzene concentration of about 300 ppm, but in actual service, this high sensitivity created difficulties due to the difference in ambient air temperatures during the hotter part of the day and cooler part of the night. The resulting false alarms were quite disturbing to the plant operators. Therefore, it was decided to sacrifice the sensitivity of the instrument in favor of a higher level alarm points of about 500 ppm. A small shelter was constructed over the analyzer unit to reduce the amount of heating due to direct sunlight, and sensitivity was thereby improved considerably. At the present time, changes are still being made in the detector to increase the sensitivity and reduce the number of false alarms. From the industrial health standpoint, as differentiated from the safety standpoint, the instrument's sensitivity is not critical. The concentrations of benzene which might be capable of producing chronic benzene poisoning are below the lowest alarm level of the instrument and health monitoring must still be done by means of the aromatic hydrocarbon detector described above. The alarm system

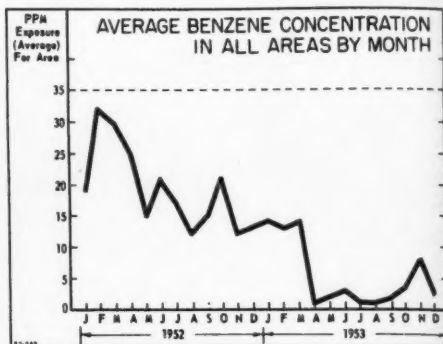


Fig. 5.
Average benzene-in-air concentrations have been progressively lowered.

EXPOSED & CONTROL GROUPS

Group	Average Hb Value	Average Urinary Sulfate Ratio
I	12.9	0.87
II	13.0	0.93
III (Control)	13.0	—

Fig. 6.
Comparison of blood and urine values with control group.

serves the primary purpose of notifying the operator of major leaks or breaks.

Conclusions

A LITTLE more than two years have elapsed since the protective program was initiated. Our laboratory results to date do not show any evidence of excessive benzene absorption by the employees. Data during the two years of operation show a very favorable trend toward the reduction of benzene concentrations (Fig. 5). A comparison of blood hemoglobin and urinary sulfate ratio averages for Group I (Benzene Plant employees), Group II (Lightly exposed group) and Group III (Control group) shows no significant differences (Fig. 6).

In spite of these encouraging signs, it is

necessary to maintain vigilance over the operations of the Benzene Plant. Complacency is the greatest problem of the future. Countermeasures such as re-education of employees, and frequent industrial hygiene and medical surveys of this problem will be a continuing part of the program.

Summary

A PROGRAM for the protection of the health of refinery employees, against acute and chronic poisoning from benzene produced in petroleum refining, is described. Protective measures include air analyses for benzene concentrations, blood and urine studies of employees, education of employees and engineering control of potential exposure points.

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Reprints Available

TWO PAPERS by W. C. L. HEMEON and GEORGE F. HAINES, JR., entitled "The Magnitude of Errors in Stack Dust Sampling," and "A New Method for Stack Dust Sampling," have recently been published. Both papers represent a part of a research program on air pollution at the Industrial Hygiene Foundation which has been supported by the American Iron and Steel Institute. Two other papers, "Exhaust for Hot Processes," and "Theoretically Required Exhaust Rates for Dust Control in Bulk Material Handling Systems," have been reprinted from chapters in MR. HEMEON'S book, *PLANT AND PROCESS VENTILATION*, released by The Industrial Press. Reprints of all four papers are available without charge by writing the Industrial Hygiene Foundation of America, Inc., Mellon Institute, 4400 Fifth Avenue, Pittsburgh 13, Pennsylvania.

INDUSTRIAL HEALTH

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CONSULTATION and RESEARCH

AIR POLLUTION
INDUSTRIAL HYGIENE
AND
TOXICOLOGY

TRACE ELEMENT
AND
MICROCHEMICAL
ANALYSES

Determination of Ethylene Oxide in Air

EXPERIENCE IN THE USE OF LUBATTI'S METHOD

R. L. HOLLINGSWORTH and B. F. WALING
The Dow Chemical Company, Midland, Michigan

A SATISFACTORY analytical method for the determination of ethylene oxide in air was required for use in chronic vapor toxicity experiments and in industrial hygiene work. A survey of the literature indicated that the method of Lubatti¹ offered the best possibility of success. It is hoped that a record of our experience with this method will prove useful to other workers.

Material Used

ETHYLENE oxide is a water-soluble, colorless gas with a sweetish odor. The boiling point of the material is 10.7° C. at normal atmospheric pressure (760 mm. of Hg) and its specific gravity is 0.887 at 7/4° C. The explosive limits of the compound are 3% to 100% by volume in air.

Two 200-pound steel cylinders of commercial grade ethylene oxide assaying 97.0-98.6% by weight by chemical and mass spectroscopic analysis were used in these experiments. Maximum amounts of the only impurities found by mass spectroscopic examination were 2.3% air and 0.7% acetylene by weight.

Gas Chamber Setup

THE THREE gas chambers employed were rectangular galvanized sheet-metal boxes. Each chamber had a volume of about 1760 liters and was equipped with a 30-inch circulating fan. Air was drawn through each chamber by means of a large vacuum pump and was exhausted outside the building. A constant rate of flow of air was maintained by use of a large Fischer and Porter Rotameter.

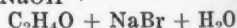
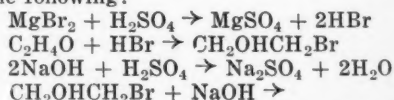
The calculated vapor concentration of ethylene oxide was maintained by pumping a known volume of the gas at a constant rate directly from a saran plastic bag reservoir into the chamber airstream by means

of a Dual Syringe Feeder Pump.² The ethylene oxide was mixed with air in a glass mixing flask before entering the chamber. Tygon tubing connections were used and the barrels of the 50-cc. syringes were lubricated with Dow Corning 550 Fluid to prevent possible leakage.

Analytical Method

GENERAL:

The analytical method employed was that proposed by Lubatti in which air containing ethylene oxide is bubbled through a dilute sulfuric acid solution containing a high concentration of magnesium bromide. Ethylene bromohydrin is formed and sulfuric acid is consumed in the process. The unused acid is then titrated with standard sodium hydroxide solution and the quantity of ethylene oxide equivalent to the amount of sulfuric acid consumed is calculated. The reactions which are believed to occur are the following:



The last reaction, showing how ethylene oxide may be regenerated from ethylene bromohydrin by sodium hydroxide, is not significant if a high bromide concentration exists in the solution being titrated.

REAGENTS:

1. Approximately 0.025 N sulfuric acid-magnesium bromide reagent. Weigh 600 gm. of pure $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ into a liter volumetric flask. Pipette 25 ml. of standard 1 N sulfuric acid into the flask and dilute to volume with distilled water.

2. Standard 0.025 N sodium hydroxide.

3. Xylene cyanole-methyl orange indicator. Dissolve 2 gm. of methyl orange and

2.8 gm. of xylene cyanole in one liter of 50% alcohol.*

PROCEDURE:

By means of a Normax pipette, 25.0 ml. of 0.025 N sulfuric acid-magnesium bromide reagent was introduced into an Ace fritted glass absorber of B porosity. The absorber had a length of 11 inches and an internal diameter of $1\frac{3}{8}$ inches. Samples of the chamber atmosphere were drawn through the absorber at a constant sampling rate of 1.0 to 1.1 liters per minute for 20-45 minutes by means of a small electric vacuum pump. The sampling rate was controlled by an orifice flow-meter which had been calibrated against a wet test meter. Blanks were run under the same conditions in the same manner from another chamber of the same size containing the same number of air-exposed control animals in order to compensate for the effect of volatile alkaline impurities given off by the excreta of animals.

A 5-ml. aliquot of the solution in the absorber was pipetted into a small Erlenmeyer flask, two drops of xylene cyanole-methyl orange indicator were added and a titration with standard 0.025 N sodium hydroxide solution was carried out. The blank was treated in like manner and the results were calculated.

CALCULATIONS:

Let A = ml. of sodium hydroxide solution required for the sample.

Let B = ml. of sodium hydroxide solution required for the aerated blank.

Then, for a 5 ml. aliquot:

$(B-A) \times N \times 44.05 \times 5 = \text{mg. ethylene oxide in sample.}$

EFFICIENCY:

Before conducting analyses for any material, it is necessary to establish that the method employed can be relied upon. Therefore, the efficiency of the method herein described was investigated by the following procedure:

*Available from Distillation Products Industries, Eastman Organic Chemical Department, Rochester 3, New York.

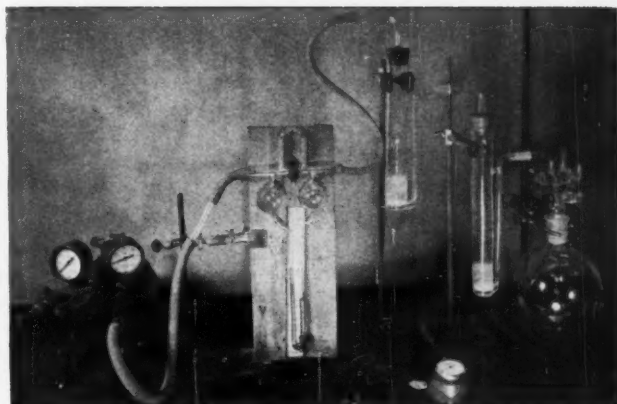


Fig. 1.

Apparatus for determining efficiency of absorption of ethylene oxide.

A small sample (7-12 mg.) of liquid ethylene oxide was introduced into a weighed, cooled, Pyrex glass bulb 8-10 mm. in diameter with a $1\frac{1}{2}$ inch capillary stem by means of a cooled 1-cc. Tuberculin syringe and a 23 gauge 2-inch needle. The tip of the stem of the glass bulb was sealed off with a small hot torch while the bulb was covered with dry ice. The bulb was weighed again after being allowed to come to room temperature. Then the weighed sample of ethylene oxide was introduced into a 2-liter 29/42 standard taper round bottomed flask. Next, the flask was stoppered with a ground glass top to which was attached a 1.5-mm. capillary dip tube with a closed 1.5-mm. standard taper stopcock and a closed 4-mm. Y bore stopcock with a 12/30 standard taper male joint welded on at a right angle. The glass bulb was shaken vigorously against the sides of the flask until the bulb broke.

The flask was then connected to two absorbers in series, each of which contained

TABLE I.
DATA ON EFFICIENCY OF METHOD

Sample No.	Wt. of Sample of Ethylene Oxide in mg.*	Mg. Recovered in First Absorber	Mg. Recovered in Second Absorber
1	7.8	7.4	0.8
2	9.0	7.7	0.8
3	11.4	10.2	0.7
4	10.7	9.9	0.7

*Corrected for 98.6% by wt. assay of ethylene oxide used.

TABLE II.
RESULTS OF ANALYSES ON AIR-ETHYLENE OXIDE MIXTURES

No. of Samples	Calculated Concentration of Ethylene Oxide in ppm	Range of Concentrations* Found by Analysis in ppm	Average Concentration of Ethylene Oxide by Analysis in ppm
23	55	82-79	49
18	113	89-157	113
15	243	168-255	204

*Concentrations are corrected for 90.6% average efficiency of absorption of ethylene oxide in the absorber used and for an aerated blank.

25.0 ml. of 0.025 N sulfuric acid-magnesium bromide reagent. Both absorbers contained an Ace porosity B fritted glass disk and had an internal diameter of $1\frac{3}{8}$ inches. The first absorber was 11 inches long and was used during the entire experimental period for sampling; the second absorber was $9\frac{1}{2}$ inches long. The Y bore stopcock between the flask and the absorbers was opened and the flask was aerated by means of a small vacuum pump and an orifice flowmeter at an airflow of 1.04 liters per minute for 20 minutes. The room air entered the flask through the capillary dip tube when the 1.5-mm. stopcock was opened immediately after starting the vacuum pump. The assembled apparatus is shown in Fig. 1.

The amount of ethylene oxide absorbed in each absorber was determined as described above. The results are shown in Table I. An aerated blank obtained under the same conditions showed the room atmosphere to be free of interfering contaminants.

From the above data it is apparent that the average efficiency of absorption of ethylene oxide in the first absorber was 90.6%. One absorber was considered adequate for use in these studies; however, for some work two absorbers would be preferable.

LIMITATIONS:

Lubatti's method for the determination of ethylene oxide is nonspecific in the presence of alkaline gases such as ammonia or acid gases such as sulfur dioxide which change the acidity of the sulfuric acid-magnesium bromide reagent. This fact does not present a problem in circumstances such as those outlined in this paper where a suitable blank correction can be made. However, for use in industrial hygiene work where a number of atmospheric contaminants are frequently encountered, due consideration must be given to the limitations of the method.

Experimental Results

THE RESULTS of analyses on various concentrations of ethylene oxide in the chambers employed are summarized in Table II.

It will be observed from Table II that the average analyzed vapor concentrations are in general agreement with the calculated concentrations. The range of the analyzed concentrations is believed to result from the combined problems of maintaining, sampling, and analyzing low vapor concentrations of a gas which is unusually reactive, readily soluble, and readily polymerizable. Future work should be directed toward the maintenance of more uniform vapor concentrations and toward the development of a more sensitive and more specific analytical method.

Summary

LUBATTI's method for the determination of ethylene oxide has been applied to prolonged, repeated vapor inhalation experiments. For calculated concentrations of 55, 113, and 243 ppm, the average concentrations determined by analysis were 49, 113, and 204 ppm, respectively.

Lubatti's method of analysis for ethylene oxide is nonspecific in the presence of alkaline or acid gases which change the acidity of the sulfuric acid-magnesium bromide reagent employed. A suitable blank correction must be applied if required, and the necessity for such a correction may limit the usefulness of the method in industrial hygiene work.

Procedures for obtaining a known vapor concentration of any gaseous material have been described.

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Determination of Small Quantities of Isophorone in Air

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ISOPHORONE (3,5,5-trimethyl-2-cyclohexene-1-one) is used principally in industry as a solvent for various resins. Inasmuch as the methods of applying resin finishes containing isophorone may at times result in excessive vapor concentration in the work room air, a reliable method for its determination in low concentrations is desirable, even though the vapor pressure of isophorone is low and its vapor has a readily detectable odor. The maximum allowable concentration for repeated eight-hour exposures to isophorone is given as 25 parts per million by volume in air in the 1954 listings of the American Conference of Governmental Industrial Hygienists.¹

The analytical procedure described in this paper involves the use of a reagent of phosphomolybdic acid in acetic acid and is specific for isophorone in the presence of methyl ethyl ketone, methyl isobutyl ketone, and acetone, solvents normally used in conjunction with isophorone. The method is particularly suited to the determination of one to 150 parts per million of isophorone by volume in air. A procedure for the continuous preparation of known concentrations of isophorone in air is also presented.

The heteropolyacids, phosphomolybdic and phosphomolybdotungstic, have been employed by several investigators for the colorimetric determination of various organic compounds capable of reducing the reagent to molybdenum blue.^{2-6,8} Folin and Wu⁴ described the preparation and use of phosphomolybdotungstic acid for the determination of blood glucose and other reducing sugars. Campbell³ determined dihydroxyacetone by the Folin and Wu reagent while Heard and Sobel⁵ found that corticosteroids reduced the Folin and Wu reagent in acetic acid medium.

Burstein² studied various conjugated un-

saturated compounds capable of reacting with phosphomolybdic acid in acetic acid medium and showed that the ability of the unsaturated compounds to reduce the reagent increases with an increase in the number of conjugated double bonds in the molecule.

The determination of olefinic-type hydrocarbons in air employing sodium molybdate-palladous sulfate reagent in a sulfuric-acetic acid medium was described by McPhee.⁷ A similar reagent impregnated on a gel for the determination of carbon monoxide in air was used by Shepherd⁹ while Polis, *et al*⁸ employed a reagent of phosphomolybdic acid and palladous chloride for the determination of carbon monoxide in air.

Isophorone was found to react with phosphomolybdic acid in acetic acid medium. No previous methods for the determination of isophorone were found in the literature.

Reagents

1. Phosphomolybdic acid.
2. Glacial acetic acid.
3. Isophorone (98% minimum purity as determined by reaction with hydroxylamine).
4. Phosphomolybdic acid reagent. Dissolve 10 gm. of phosphomolybdic acid in 100 ml. of glacial acetic acid and filter through No. 42 Whatman filter paper to remove any undissolved material.

Sampling Procedure

TWENTY ml. of glacial acetic acid were transferred to the sampling flask of a Mine Safety Appliances Company Midget Impinger air-sampling apparatus equipped with a fritted-glass bubbler of fine porosity. The sampling flask was attached to the sampling outlet of the apparatus shown in Fig. 1. A sampling rate of one liter per

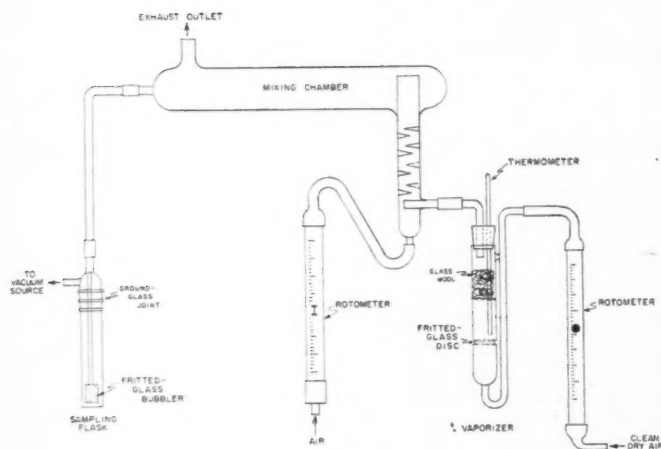


Fig. 1.

Apparatus for preparing known mixtures of isophorone in air.

minute for five minutes was used. Because some evaporation of the scrubbing solvent was encountered during sampling, the volume after sampling was not always 20 ml.

Procedure

THE TOTAL volume of the scrubbing solvent after sampling was noted. The amount of scrubbing solvent solution indicated in Table I was transferred to a 25-ml. glass-stoppered graduated cylinder. Sufficient glacial acetic acid was added to dilute to 10 ml. One milliliter of the phosphomolybdic acid reagent was added by pipet and the cylinder was shaken to mix the contents and placed in a boiling water bath for 45 ± 5 minutes. After allowing the cylinder to cool to room temperature the reaction mixture was diluted to 15 ml. with additional glacial acetic acid. The absorbance of the solution was measured against a blank in one-centimeter cells using a Beckman Model

B spectrophotometer at a wavelength of 650 $m\mu$. The blank consisted of 10 ml. of glacial acetic acid and 1 ml. of the phosphomolybdic acid reagent, heated, cooled, and diluted to 15 ml. with glacial acetic acid.

Calibration Curve

ONE-TENTH of a gram of isophorone was accurately weighed into a 500-ml. volumetric flask and diluted to 500 ml. with glacial acetic acid (Dilution A). Five milliliters of this dilution were diluted to 100 ml. (Dilution B).

Two, four, six, eight, and 10-milliliter aliquots of Dilution B were transferred to respective 25-ml. graduated cylinders and diluted to 10 ml. with glacial acetic acid. These were then subjected to the same procedure as described above for the sample. A plot of absorbance versus micrograms was made. Each milliliter of Dilution B contains the following number of micrograms of isophorone: 100 times the number of grams of isophorone added in Dilution A.

Calculation

$$\frac{A \times B \times F}{0.84 \times 138 \times C \times D} = \text{isophorone, ppm by volume in air}$$

A = micrograms of isophorone in aliquot from calibration curve

B = total ml. of scrubbing solvent before analysis

C = ml. of scrubbing solvent used for analysis

D = liters of air sampled

$$F = 22.4 \times \frac{273 + t}{273} \times \frac{760}{p} = \text{liters per}$$

mole at atmospheric pressure and temperature

0.84 = experimentally determined scrubbing efficiency

138 = molecular weight of isophorone

TABLE I.
SAMPLE SIZE OF SCRUBBING SOLVENT FOR
VARIOUS CONCENTRATION RANGES OF
ISOPHORONE IN AIR

Estimated isophorone content, ppm by gas vol.	Aliquot of acetic acid scrubber, ml.
1 to 8	10
4 to 40	5
8 to 80	1
40 to 400	0.5

Results and Discussion

A RATE STUDY of the reaction of isophorone with the phosphomolybdic acid reagent showed that a period of 40 to 50 minutes at steam bath temperature was necessary for reproducible color development. A further study showed that the reaction must be carried out at the temperature of boiling water in order to obtain consistent results.

A scan of absorbance versus wavelength is shown in Fig. 2 for a blank and a sample against distilled water. As will be noted, two peaks in absorbance were found, one at 650 $m\mu$ and the other at 870 $m\mu$. Although the 650- $m\mu$ wavelength was used in this work, if greater sensitivity is desired, a wavelength of 870 $m\mu$ may be employed. Calibration curves of absorbance versus micrograms of isophorone contained in 10 ml. of glacial acetic acid are plotted in Fig. 3 at both wavelengths, 650 and 870 $m\mu$.

Known concentrations of isophorone in acetic acid were prepared and analyzed in order to determine the accuracy of the method of analysis. The results are indicated in Table II.

Inasmuch as in this investigation an optimum accuracy was found at an absorbance range of 0 to 0.5 at 650 $m\mu$, suitable dilution of the scrubbing solvent was necessary for higher concentrations of isophorone in the air samples. The total volume of the scrubbing solvent was noted after each sampling. A suitable aliquot was then taken and diluted to 10 ml. before analysis was started. Table I shows the volume of the aliquot used for various concentrations of isophorone.

Preparation of Air Samples

THE APPARATUS shown in Fig. 1 was used to prepare samples of known concentration of isophorone in air. The vaporizer, which was equipped with a fine fritted-glass

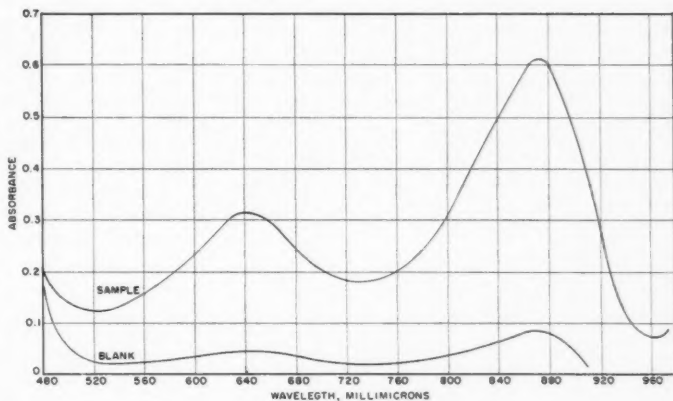


Fig. 2.

Isophorone, reaction with phosphomolybdic acid in acetic acid, wavelength vs absorbance. Reaction conditions: 45 ± 5 minutes at $98 \pm 2^\circ \text{C}$. Comparison made against distilled water.

disc for maximum isophorone-air contact, was charged with isophorone and accurately weighed. After the vaporizer was assembled in position, clean, dry air was passed through it at a rate of 1500 cc. per minute. The time at which the vaporization was started was noted. The dilution air was ad-

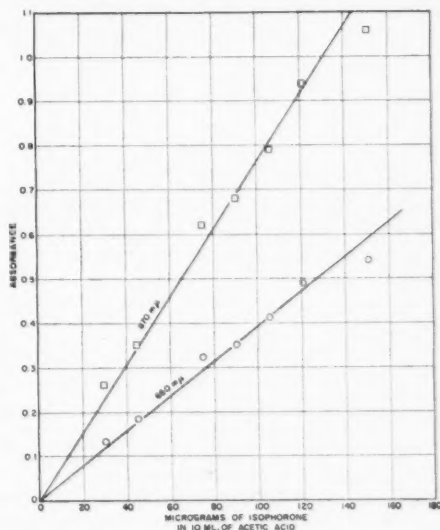


Fig. 3.

Calibration curves: Isophorone in acetic acid using phosphomolybdic acid reagent. Readings at 650 and 870 $m\mu$.

TABLE II.
EVALUATION OF METHOD OF ANALYSIS USING
KNOWN CONCENTRATIONS OF ISOPHORONE IN
ACETIC ACID

Isophorone, micrograms		Difference
Added	Found	
12	11	- 1
12	12	0
12	15	+ 3
14	17	+ 3
26	32	+ 6
28	30	+ 2
29	29	0
31	31	0
31	40	+ 9
46	48	+ 2
50	44	- 6
50	52	+ 2
52	60	+ 8
56	58	+ 2
58	48	-10
62	58	- 4
62	53	- 9
62	56	- 6
62	57	- 5
70	75	+ 5
78	85	+ 7
87	72	-15
93	80	-13
93	87	- 6

Standard deviation = 4.1 micrograms over the range of 12 to 93 micrograms.

justed at a fixed rate of 2 cu. ft. per minute, and approximately 30 minutes were allowed for the air-isophorone mixture to come to equilibrium. Samples were then taken at this concentration level. The dilution air was then decreased and after again allowing 30 minutes for equilibrium at this new dilution-air rate, samples were again taken. By varying the dilution air rate in small increments from 2 to 0.2 cu. ft. per minute, synthetic air samples from 4 to 37 ppm were prepared. The vaporizer air was then stopped, the time lapse since the start of vaporization noted, and the vaporizer was reweighed. The following calculation was used to obtain the isophorone content in the effluent air:

W

$$\frac{W}{MW} \times MV \times 10^6$$

MW

= isophorone,

(T x VAR) + (T x DAR)
ppm by gas volume

W = weight loss of isophorone in the vaporizer, gm.

MW = molecular weight of isophorone = 138

MV = mol value (22.4 liters/mole correct-

ed for temperature and pressure)

VAR = vaporizer air rate in liters per minute

DAR = dilution air rate in liters per minute

T = total time lapse of vaporization, minutes

A compilation of data showing the analysis of samples of known isophorone concentration is shown in Table III. Since the calibration curve for isophorone in acetic acid had previously been established, the average recovery of 83.9 per cent was the scrubbing efficiency of the solvent under the sampling conditions of one liter per minute for five minutes. By correcting all the analyses for this scrubbing efficiency, the data shown in Column 5 (Table III) resulted.

Inasmuch as methyl ethyl ketone, methyl isobutyl ketone, and acetone are normally used in conjunction with isophorone, the method of analysis must not be affected by these solvents.

TABLE III.
ANALYSIS OF AIR SAMPLES OF KNOWN
ISOPHORONE CONCENTRATION

Sample number	Parts per million by gas volume		Per cent recovery (scrubbing efficiency)	Parts per million found corrected for scrubbing efficiency, 83.9		Difference in ppm (Col. 2-5)
	Added	Found				
1	11	9.9	89	12	-1	
2	5	4.8	96	6	-1	
3	8	7.5	94	9	-1	
4	25	24.3	97	29	-4	
5	4	3.6	90	4	0	
6	5	4.0	80	5	0	
7	7	5.9	85	7	0	
8	7	5.2	74	6	+1	
9	11	8.3	76	10	+1	
10	11	6.6	60	8	+3	
11	19	12.8	67	15	+4	
12	33	26.2	80	31	+2	
13	37	28.1	76	34	+3	
14	20	17.5	88	21	-1	
15	12	10.9	91	13	-1	
16	8	6.4	80	8	0	
17	5	3.8	85	5	0	
18	3	3.1	103	4	-1	
Ave. = 83.9						

Standard deviation = 1.4 ppm over the range of 3 to 37 ppm.

Samples of these ketones were prepared by adding known amounts directly to acetic acid and analyzed as described for isophorone. It was found that a concentration of 10,000 micrograms of each of these com-

pounds gave a color intensity equivalent to approximately 10 micrograms of isophorone. Therefore 1000 ppm of each ketone would give an apparent isophorone content in air of 1 ppm. Interference due to carbon monoxide is negligible up to at least 300 ppm.

Summary

AN ANALYTICAL procedure is presented for the colorimetric determination of small quantities of isophorone in air by reaction of an air sample, scrubbed through glacial acetic acid, with phosphomolybdic acid. The resultant molybdenum blue reaction product is measured spectrophotometrically. A pro-

cedure for the continuous preparation of samples of known isophorone content in air is also presented.

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Distinguished Service Citation



Preceding the formal opening of the 15th Annual Congress on Industrial Health, held in Washington, D.C. on January 25 and 26, 1955, Dr. Walter B. Martin, President of the American Medical Association, presented the Distinguished Service Citation to the Occupational Health Program of the Public Health Service, U.S. Department of Health, Education and Welfare, for its outstanding contribution to the protection and improvement of worker health. Dr. Seward E. Miller, who had directed the Occupational Health Program for the past five years, accepted the award in the name of all those who had been associated with this activity in its 40 years. At right is Dr. Leonard A. Scheele, Surgeon General of the Public Health Service.

Alpha Hazard Monitoring Instruments

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Occupational Health Field Station, Division of Special Health Services
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THE ESTIMATION of area contamination by alpha-emitting radioactive elements is a problem that used to be of interest only to those individuals handling unencapsulated radium, such as workers in radium refineries and dial painting establishments. However, the production and use of alpha-active elements has risen to the point that many thousands of workers are now handling these materials, with a consequent increase in contamination potential. For this reason, it was felt that a discussion of the instruments used to detect and evaluate health hazards from alpha-emitting elements should be included in this symposium.

Only those instruments which are readily available and which are suitable for use in the field will be discussed. This does not mean that laboratory instruments have solved all problems connected with the laboratory measurement of alpha particles, and that therefore laboratory problems do not need to be considered, but rather that, at this time, field problems are more difficult to solve.

Since the measurement of low energy beta particles presents many of the same difficulties encountered in the measurement of alpha particles, many of the comments concerning alpha hazard monitoring will also apply to beta radiation.

The measurement of alpha particles requires a thorough comprehension of their properties, as well as a knowledge of the characteristics of the instrument used. Therefore, it may be desirable to review those properties which are of special importance.

As we know, alpha particles are short-range and have quite low penetrating power compared with beta particles or gamma

rays. This means that monitoring instruments must have very thin windows in order to admit alpha particles at all. Also, instead of being a negligible item, air absorption is an important factor in alpha measurements.

The second important characteristic of alpha particles is that they have a high specific ionization as compared with beta particles or gamma rays. This is one property that enables the instrument designer to construct instruments that will specifically measure alpha particles even in the presence of large amounts of either beta or gamma radiation.

These properties of alpha particles mean that it is necessary to use extreme care in taking measurements in order to obtain reproducible and interpretable data. The geometry of the situation is all-important, and slight changes in source to instrument distance, or the introduction of small amounts of absorbing material, such as a thin layer of dust, will introduce large variations in the instrument readings. Throughout the following discussion of instruments, these characteristics should be kept in mind to see how they affect instrument behavior.

Available Instruments

INSTRUMENTS suitable for alpha hazard monitoring utilize the same principles that are followed in other radiation measuring devices. Ionization chamber instruments, proportional counters, Geiger counters, and scintillation counters can all be used with the appropriate changes in construction details.

Ionization chamber instruments are designed to take advantage of the high specific ionization and short-range of alpha particles to differentiate them from betas or gammas. This is done by making the chamber shallow enough so that relatively

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little ionization will be produced in it by beta particles, while the alphas will expend most of their energy in the chamber. The chambers are either windowless or are equipped with a very thin window in order to admit the alphas to the chamber without serious energy losses. If the ionization current is then fed through an integrating circuit to a meter, we have a device which can under some circumstances give readings that can be interpreted in terms of counts per minute. Such ionization chamber rate meters can be obtained varying in sensitivity from those that will detect a few alphas per minute to those that require several million alphas per minute to give measurable meter readings. Quartz fiber electroscopes with thin windows or no windows will, of course, do exactly the same work as is done by the electronic devices, since they operate on the same basic principle-measurement of ionization current.

Field type proportional counters also use shallow chambers to increase their selectivity for alpha particles, and the circuits are designed to reject pulses below selected voltages. Again, the resulting current is fed to a meter which will give a reading proportional to the current which it receives.

Geiger counter survey meters equipped with thin end window tubes are available and so can also be used for alpha survey work. The sensitivity of such devices is comparable with that of the more sensitive ion chamber instruments. Differentiation between alpha particles and other types of radiation must be accomplished by the use of absorbers.

Scintillation counters designed to measure alpha particles are hardly a production item at this time, but they should be mentioned for the sake of completeness. By a proper selection of crystals and operating voltages, it should be possible to obtain good selectivity for alphas and good signal to noise ratios in such instruments. The necessary light tight covering for crystal would introduce a rather thick absorber which would reduce the sensitivity of the counter.

These descriptions of instruments which may be used for alpha monitoring are quite brief, and are only intended to point out the items which must be considered in selecting instruments to use in studying

any particular situation. The exact behavior of any instrument can be deduced from the manufacturer's design data, or can be determined by experiment.

Now that we have glanced over the list of available instruments, we should consider the use to which these devices will be put. The primary use for alpha monitoring instruments has been to perform area surveys to determine the presence or absence of contamination on surfaces, and, if possible, to estimate the level of activity. The first objective is easily reached since all of the devices that have been mentioned are sensitive to alpha particles and will indicate their presence. However, to settle the second point requires more effort on the part of both the instrument and the operator. Attempts to use survey instruments to measure quantitatively the amounts of alpha-emitting elements present on a surface will be unsuccessful except under certain exceptional circumstances. Anyone who has had much experience in monitoring for alpha contamination knows that this situation exists and can tell when it might be possible to make quantitative measurements and when qualitative data will have to suffice. However, it may not be too time-wasting to review the items that must be kept in mind when working with alpha particles.

The first important detail to consider is that, with the exception of Geiger tubes, all of the devices which have been discussed are energy dependent. Whether the detecting mechanism consists of an ion chamber, a proportional chamber, or a scintillation crystal, the current produced is fed into an ammeter. This means that the size of the initial event in the detector will affect the reading on the meter. For example, a uranium alpha with an energy of 4.2 mev will not register the same on a meter as will a RaC' alpha whose energy is 7.7 mev. Calibration of each particular instrument against the exact material that is the expected contaminant is therefore imperative. Sometimes considerable ingenuity is required in order to establish calibration procedures that will yield data valid for the problem at hand. Standards for calibration are not always available, and therefore it may be necessary to cross-check the survey meters with a laboratory alpha counter,

using a known amount of the element to be assayed as a working standard.

Another extremely important point to consider is the manner of deposition of the alpha-active material. If the contaminated surfaces are not absorbent, no problem exists, and one can proceed with the survey. However, if the contaminants are on surfaces which have allowed the radioactive material to penetrate to varying depths, the situation is nearly hopeless. The range of alpha particles in matter is so short that if there has been any penetration into the surface, the particles that reach the detector will have energies varying from just enough to reach the sensitive volume of the instrument to the maximum theoretical energy. Under such circumstances, the best the instrument can do is to indicate a reading, and the best the monitor can do is realize that the circumstances do not permit any quantitative evaluation of the situation.

In the preceding discussion, it has been tacitly assumed that the hazard that is being investigated is created by a single element. Wherever natural radioactive materials, such as radium, uranium, or thorium ores, are being handled, there will be a number of different alpha-emitting elements present, and even if they are deposited on nonabsorbent surfaces the situation will be confusing. For example, consider a case where radium has been spilled. It is quite difficult to make a radium preparation that will freely emanate all the radon that is formed. Therefore, very shortly, four different energy alpha particles will be emitted from the area where the radium was deposited, with the ratio between them depending on the amount of radon that is retained and the length of time that the material has been in place. Here, it would be difficult to interpret instrument readings to give the amount of radium actually present. Semi-quantitative information is about the best that can be obtained with most mixtures of elements.

So far, area monitoring for surface contamination has been the only field considered. Probably the determination of airborne radioactive dust is of much more significance from a health standpoint than is surface contamination. As long as alpha-emitting elements remain on surfaces, they are not particularly hazardous. When they

become airborne, however, it is certain that some of the material will be inhaled and will be retained in the body, where a definite health hazard will be created.

The techniques of collecting dust have been fully discussed elsewhere in this symposium and therefore need no repetition here.

If possible, the sample should be secured by filter paper methods. Self-absorption factors for filter papers can be determined, and the subsequent determination of radioactivity will not be unnecessarily complicated. For most radioactive materials, the maximum permissible levels for atmospheric contamination are so low that laboratory methods are required to analyze air samples. However, where radioactive ores are being handled, the levels of activity are high enough to permit evaluation of the samples with field instruments.

This discussion was supposed to be primarily concerned with instruments, but it has developed to be a description of methods with the devices taking a position of secondary importance. Frankly, this is the way that most of the alpha-monitoring problems which we have encountered have developed. On the basis of our experience, it seems that the principal requisite for obtaining useful results from alpha survey instruments is that the user have a good understanding of the design characteristics and method of operation of the particular device which is available and of the nature of the problem being investigated.

Summary

THE VARIOUS pitfalls that may be encountered during the course of an alpha-monitoring survey have been discussed. The information that can be obtained has also been pointed out, and some consideration has been given to instrument design. To summarize all of this, it seems that the following conclusions can be made:

1. Alpha-monitoring instruments are capable of giving quantitative data under some special circumstances, such as in measuring air-borne radioactive dust, or in surveying nonabsorbent surfaces which are contaminated with a single alpha-active element.

2. If the area in question is contaminated with a mixture of alpha-active elements, or if the surface is adsorbent, only semi-

quantitative or qualitative measurements can be obtained.

As a general conclusion, it can be said that alpha-monitoring instruments based on all the different principles that have been used in making radiation measuring equipment are available or can be constructed. The exact choice of instrument for any particular situation should depend on such practical factors as initial cost, ease of

maintenance, and the sensitivity needed. Inherently, no type of device has overall advantages over any other type. For example, in many situations, an electroscope will do as satisfactory work as will the most complex instrument on the market. Again, it must be emphasized that an understanding of the situation is the primary prerequisite in evaluating hazards from alpha-emitting elements.

Program on Noise Reduction

A TWO-WEEK Special Summer Program on Noise Reduction, designed to present the latest developments in the field will be offered at the Massachusetts Institute of Technology, commencing Monday, August 15 through Friday, August 26. This present Program is directed to engineers with a noise problem rather than to acoustical experts. The Program will start with demonstrations of methods for measuring noise of several types using survey meters, octave band analyzers, peak reading meters, magnetic tape recorders and cathode-ray oscillographs. The Program will be under the direction of PROFESSOR LEO L. BERANEK, Associate Professor of Communications Engineering, assisted by members of the staff of M.I.T.'s Acoustics Laboratory and by other invited guest lecturers. Information and application blanks may be obtained from: PROFESSOR ERNEST H. HUNTRESS, Room 7—101, Massachusetts Institute of Technology, Cambridge 39.

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Training Industrial Hygiene Chemists in Latin America

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THE INSTITUTE of Inter-American Affairs, an agency of the United States government, has been cooperating in public health activities with the national governments of Latin America since early 1942. In each country, the joint program is carried out through an agency set up for the purpose, usually known as *El Servicio Cooperativo Interamericano de Salud Pública* (Inter American Cooperative Public Health Service).

These cooperative programs originated in resolutions adopted at the conference of American Foreign Ministers held at Rio de Janeiro in January, 1942 to the effect that health and sanitary measures were basic to the hemisphere's defense, but since public health programs are fundamental to the general defense against disease, they have been continued at the request of the cooperating countries. Today, cooperative public health programs are being carried out in nearly all the Latin American countries by the Ministries of Health of the national governments and the Institute of Inter-American Affairs of the United States government. The Institute of Inter-American Affairs functions as the Inter-American Regional Office of the Foreign Operations Administration.

Under these programs, hospitals, health centers, water supplies, sewerage systems, and other health and sanitary facilities have been constructed. Numerous projects have been undertaken in preventive medicine against major disease problems. A large number of public health technicians has been trained, many of whom have been allotted grants from the Institute of Inter-American Affairs for study in the U.S.

The first activities in industrial hygiene were begun under these programs late in 1945, when the Bolivian government requested that someone be sent to study the serious health problems among Bolivian workers, particularly those employed in the strategic tin mining industry. The first industrial hygiene program which the North American technicians have helped to create was the one in Peru, where training of personnel was started late in 1948. At that time, the Institute of Inter-American Affairs assigned to this country an engineer and a chemist, both specialists in industrial hygiene, who were responsible for building up a modern industrial hygiene department, which could function as a service to Peruvian industries. An industrial hygiene laboratory was begun in 1948, and the first Peruvian chemists employed by the Department of Industrial Hygiene went in training under the direction of the consultant chemist.

Due to an awakening interest in industrial hygiene among the various countries in Latin America, an interest largely brought about by the trend toward industrialization, a definite technical assistance program in this branch of public health was established under the general cooperative program late in 1950. Headquarters for this activity were established in Lima, Peru, since this country was well advanced in the field by that time, and also since it is so located geographically that consultants can easily travel to other countries as needed. Requests for assistance came from all directions, and the U.S. technicians have helped to create the programs now operating in Bolivia, Brazil, Chile, Colombia, Mexico,

Peru, and Venezuela. Consultants in industrial hygiene are assigned to all but two (Chile and Mexico) of these countries. A technician served as advisor in Chile during the first three years of the program and then was transferred to another country.

Quite early in our work, we recognized that chemists from other countries would have to be trained at the Lima laboratories and such training was established in 1951. This was done in order to avoid the language barrier and also because there is no school in the United States offering an intensive course in industrial hygiene chemistry such as was needed for the Latin American chemists picked for the new programs.

We soon learned that the chemists in Latin America are, as a rule, adequately prepared from the theoretical point of view, but because of the lack of suitable equipment receive very little practical training in laboratory techniques. This is especially true with respect to the instrumentation on which modern chemistry relies.

In our work in Latin America, we are utilizing instrumentation for many phases of industrial hygiene and have emphasized the creation of laboratories around two particular methods of instrumentation, that is, the polarograph and the spectrophotometer. These have been selected because they are time-saving, facilitate remote supervisory control, and because of reproducibility of accuracy. Industrial hygiene chemistry, as taught here, is really pioneering work in this part of the world, since there has been little experience with these types of instruments in the majority of the laboratories in the countries where we have worked so far.

Prior to the introduction of instrumentation in chemical laboratories, the number of samples that could be taken in the field were definitely limited by the manual capacity of the laboratory. Today, in Peru, where we have the oldest industrial hygiene laboratory in Latin America, the field personnel think nothing of bringing back 500 or even 1,000 samples, because with the methods which have been developed utilizing instruments it is possible to handle this number of samples rapidly, accurately, and with a minimum error in the evaluation of toxic constituents.

We have had to work out our own course of training for chemists in industrial hygiene in Latin America, using as our base the methods adopted by the American Conference of Governmental Industrial Hygienists, which have been translated into Spanish. The trainees who spend anywhere from six months to a year at the Lima laboratories, depending on their previous background, are thus able to follow written, as well as oral, instructions in their own language. Each trainee is given both theoretical and practical work in the laboratory, with emphasis on polarography and spectrophotometry.

When a chemist has completed his basic training at Lima, he returns to his own country, and the consultant in industrial hygiene chemistry soon visits the trainee in his own laboratory to assist him in setting it up and in standardizing his procedures.

Visits to each country are made by the consultant at least once a year to assist the chemist in solving difficult and exceptional problems and also to evaluate his progress. Evaluation samples are submitted to each chemist in accordance with ACGIH standard procedure. The consultant in industrial hygiene chemistry also keeps his former students informed on current developments by circulating a newsletter on latest techniques in the field.

To date 13 standard methods, representing 10 different elements and compounds, have been prepared in accordance with the common or specific needs of each program. Of these, two are ACGIH procedures for the determination of mercury and oxides of nitrogen, which have been translated into Spanish, with the addition of the Ringbom optimum range data which are considered important.¹ For the analysis of free silica and biological vanadium, Talvitie's method is used.² For cadmium analysis in biological samples the method of Saltzman is employed.³ To both of these methods has been added optimum range information.

The polarographic determination of lead, cadmium and zinc in atmospheric samples has been developed using 30% calcium chloride as the supporting electrolyte, as suggested by Khlopin.⁴ The balance of the procedures including methods for biological antimony,⁵ atmospheric formaldehyde,⁶ bi-

ological arsenic,⁷ and lead,⁸ are all well known procedures, such as the Bambach lead method.

In addition, we are now working in the Lima laboratory on polarographic manganese procedure, which is almost completed, and have initiated an investigation on the polarographic determination of selenium and tellurium in atmospheric samples, which is of interest to the Colombian program.

Some work has also been done on the amperometric determination of fluorine as well as on the various spectrophotometric procedures recommended for this element. This field of interest will be pursued more extensively in the near future.

Each trainee acquires training and experience in each of the above mentioned procedures through the preparation of his own standard curve, duplicating the accepted master curve, and prepares his folder of standard procedures to take back to his country.

Once he has sufficient experience, he works on actual samples which come in from the field as a member of the Peruvian team on a given study and under the supervision of the consultant.

The format used in writing up these procedures covers the usual steps, such as references, theory, reagents, procedure, standard curve data, collection of sample, recovery, interferences, and optimum range.

Obviously, it is not possible to train a chemist completely in all the theoretical aspects of the instrumental methods of analysis, but enough information is made available to him, including adequate bibliography, to give him a sound basis of operation.

Relative to polarography, the elementary theoretical concepts such as the Ilkovic equation, and the importance of its component factors are discussed and studied. More emphasis is placed on the practical applications, including the preparation of reference electrodes such as the saturated calomel electrode, internal standard and standard addition methods, purification of mercury, calibration and selection of capillaries with predetermined characteristics, maximum suppression, supporting electrolytes, and determination of galvanometer values, to mention a few items.

In the realm of spectrophotometry, we cover the determination of spectral characteristics and optimum range, as well as the basic laws of absorption such as the Beer-Bouguer law. Also, the students are indoctrinated in the wavelength calibration of the spectrophotometer and general maintenance of the equipment which they use. This is very important in Latin America, where satisfactory technicians versed in the repair of these instruments are not readily found.

Actually, it has proven to be necessary to teach elementary microchemistry techniques to the University graduates, since there is little opportunity for the Universities to develop programs in this field.

Since there isn't a single text available in Spanish on laboratory techniques in industrial hygiene chemistry, a book on this subject is in preparation by the consultant. This book will include chapters on laboratory safety, statistics, forms, equipment lists, a model laboratory design, standard laboratory procedures, and general background information on the fields of polarography and spectrophotometry.

So far, 17 chemists have been trained at the Lima laboratories. Three of these came from Brazil, two from Mexico, one from Chile, one from Colombia, one from Bolivia, and nine from Peru. A few chemists are being sent to the United States on scholarships furnished by the Institute of Inter-American Affairs for study at a school of public health. These are usually men who are slated to become leaders in their field and need to obtain a broad public health background.

From this brief description of the methods employed in the training of chemists in industrial hygiene laboratory work it is obvious that the immediate need of providing trained chemists for the industrial hygiene programs in the various Latin American countries is being filled. However, the training which these students receive in Lima is limited to laboratory work with some field experience through the student's participation in actual studies being conducted by the Department of Industrial Hygiene. It is hoped that in the near future one of the three schools of public health which exist in Latin America will develop an industrial hygiene course which will in-

clude intensive training in laboratory procedures for chemists. When this is done, the trainee will receive, in addition to the type of instruction he can now only obtain in Lima, public health instruction, which will make him a more useful person in industrial hygiene.

When such a department of industrial hygiene at a school of public health is made available it will be possible to train more personnel, to carry on research in industrial hygiene, and to develop new

methods of analysis, so essential in a dynamic field such as industrial hygiene.

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Representatives

EDGAR C. BARNES and JAMES H. STERNER, M.D., have been appointed by HERBERT T. WALWORTH, President, AMERICAN INDUSTRIAL HYGIENE ASSOCIATION, as official representatives to the National Committee on Radiation Protection. The Association is honored by the invitation to participate in the activities of this Committee. The representatives appointed, MR. BARNES and DR. STERNER, are well qualified in the radiation field to extend a creditable service.

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The Origin of Industrial Dusts

AN X-RAY DIFFRACTION METHOD FOR DETERMINATION

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THE PRESENT popular interest in atmospheric pollution has prompted many individuals and groups to become aware of dusty conditions in their environment, and to seek improvement of these conditions. Redress is usually sought by complaint to a local governmental agency whose task it then becomes to determine the nature and origin of the dusty condition and to institute measures for its abatement. This task is often complicated by pre-conceived ideas of the complainants as to the origin of the dust. The investigator is then confronted not only with the problem of determining the origin of the dust but also of dispelling these pre-conceived ideas which are sometimes fallacious and often emotional. It readily can be seen that specific and graphic data regarding the composition and origin of atmospheric dusts would be invaluable, especially in investigations involving litigation.

In solving problems of this type, investigators have borrowed the epidemiological methods of the public health worker and the dust collection and analysis procedures of the industrial hygienist. A typical dust survey was described by Chen and Charmberty in 1949,² the results of which are shown in Fig. 1. A small industrial community was desirous of locating the source of its dust problem and to this end the survey was directed. Macro samples to be used for the determination of the nature of the dust were collected in sootfall boxes placed at various points throughout the town as shown by figures enclosed in rectangles. Dust concentration contours were plotted on the map of the town from data obtained with the midget impinger collecting device

This report describes a method for the rapid and precise comparison of x-ray diffraction patterns of industrial and atmospheric dusts. The method was developed in order to facilitate the positive determination of the origin of atmospheric dust. Once this determination has been made, the abatement of the atmospheric pollution can be more readily accomplished since the actual source can be controlled. Slight modifications of commercial instruments are necessary to permit this type of pattern comparison; these modifications are described. Two examples of the application of the method are discussed, showing the type and specificity of results that can be expected.

and Sedgewick-Rafter dust counting cells. This plot clearly showed the major dust producing areas in the community, but could not indicate the proportion of dust contributed by the various plants within the area. The latter type of information is highly important to the investigator since it will prevent his indicting an innocent plant, or allowing a culprit to escape unchallenged, either of which might prove embarrassing.

The determination of the proportional contributions by various plants to the atmospheric dust cannot readily be accomplished by chemical analysis since minerals may be chemically identical yet differ crystallographically. For example, two adjacent plants conceivably may be using microcline and orthoclase, respectively. Both these minerals are known as feldspar, and their chemical compositions are identical, though they differ crystallographically. It is also within the realm of possibility that

Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 7, 1952.

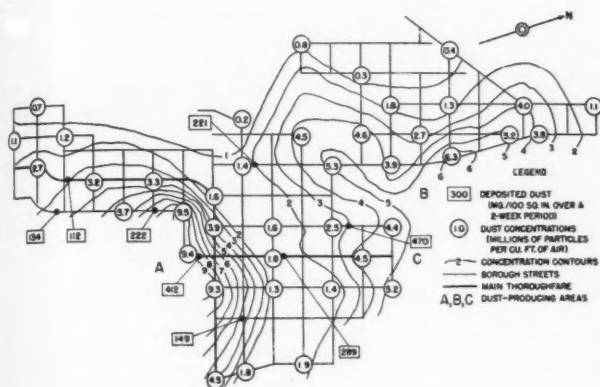


Fig. 1.

City map showing dust collection locations, dust concentrations and concentration contours. Dust producing areas as determined by this study are also shown. Reprinted from *Industrial and Engineering Chemistry*.²

adjacent plants may be using two different minerals, the mixture of which will show a chemical analysis similar to a third material.

Crystalline materials can be differentiated through their x-ray diffraction patterns. Each material produces a characteristic pattern and the pattern of a mixture is a composite of the patterns of the individual materials comprising the mixture. The intensity of the diffraction pattern is proportional to the amount of material present in the sample. By comparing the diffraction pattern of an atmospheric dust with the patterns of the materials used and produced by various plants in a dust producing area, it is possible to determine which plants are producing the dust, and by comparison of pattern intensities, what proportion of the dust is produced by each plant. A method has been suggested using photographic diffraction patterns for this type of comparative analysis of industrial dusts.^{1,2} This method requires the use of standard patterns for comparison, or the complete analysis of the unknown pattern. Atmospheric dusts, which are usually complex and may be made up of many components, do not lend themselves well to this type of analysis, since patterns of mixtures of more than three or four components are so complex as to defy analysis in many cases. If the patterns of the atmospheric dusts and those of

the various plant products could be recorded on a single medium in such a way that they were adjacent yet easily distinguishable one from another, comparative analysis would be much simpler. In addition, a careful observation of the coincidence of the various peaks would greatly facilitate complete identification of the various dusts.

Such a comparative analysis technique is possible by the use of the recording type x-ray spectrometers now available commercially with only slight modification. The instrument used in the work to be described is the North American

Phillips 90° Geiger counter x-ray spectrometer.³ It consists essentially of a source of x-rays, a Geiger tube mounted on a goniometer for the reception of the diffracted rays, and a scaling circuit feeding into a high speed recording strip chart potentiometer for automatic recording of diffraction patterns. Slits for limiting the height and width of x-ray beams are provided at the exit window of the x-ray tube and the entrance window of the Geiger tube. The specimen post is geared to rotate at one-half the angular velocity of the goniometer so that the conditions required by Bragg's law will be met. The fact that synchronous motors are used to drive the goniometer arm and the strip chart of the potentiometer is of great importance in the method to be described since this insures that the angular orientation of the goniometer arm is constantly in phase with the linear position of the strip chart.

In order to permit multiple pattern recording on a single chart, a method of displacing individual patterns is necessary so that a minimum of overlapping and superposition occurs. This can be accomplished by providing the potentiometer circuit with a bias or bucking voltage so that the diffraction pattern may be shifted in a positive or negative direction at will. The requirements of this circuit are quite strict.

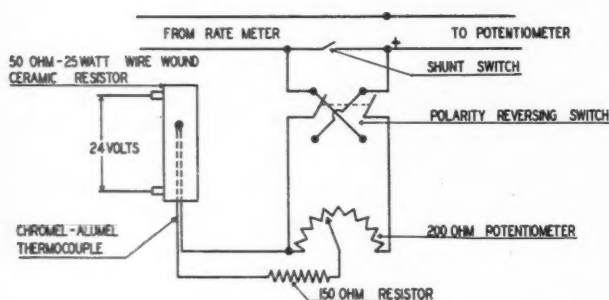


Fig. 2.

Circuit diagram of bias-bucking voltage generator and controls for adjusting pen position on x-ray spectrometer recorder strip chart.

It must not affect the intensity relationship of the pattern peaks, it must be capable of smooth regulation from 0 to full deflection, it must be stable, and it must not affect the other portions of the circuit. The type of circuit used is shown in Fig. 2. The source of voltage is a Chromel-Alumel thermocouple cemented inside a 50 ohm, 25 watt, hollow, ceramic, wire wound resistor, R1. The resistor is heated by a 24-volt alternating current supplied by a stepdown transformer, producing a potential of 9.5 millivolts at the cold junction of the thermocouple leads. One of the thermocouple leads is brought directly to one side of a double-pole, double-throw, polarity-reversing switch, the other to a 200 ohm potentiometer through a 150 ohm fixed resistor. The potentiometer is connected across the polarity-reversing switch as shown, and the circuit is placed in the positive line from the scaling circuit. A shunt switch is provided to cut out the bias-bucking circuit if desired. With the aid of this auxiliary circuit, many patterns may be recorded on a single strip chart, with all patterns exactly in phase so far as diffraction angles are concerned.

Samples are prepared first by grinding the dust to sufficient fineness to pass a 200 mesh screen. Further reduction in particle size is accomplished by grinding for two hours with ethanol in a power driven mortar and pestle. Sufficient ethanol is added so that at the end of the grinding period a thick paste remains, most of the ethanol having evaporated. The paste is then dried at 105° C. (This technique produces a powder having an average particle size of

one to three microns, with a maximum of about five. A particle size of five microns or less has been found necessary to prevent preferred orientation of the crystal fragments in the sample mount.⁴ Such preferred orientation would negate the characteristic intensity relationships of the diffraction peaks.) One-half gram of this powder is then mixed with an equal amount of Dow-Corning "Silicone" stopcock grease

and the resulting mixture is placed in a specially prepared slide, Fig. 3. The surface of the sample is leveled and made coincident with the plane of the slide by scraping with a glass microscope slide. This type of preparation greatly facilitates handling of the sample, allows a smooth specimen surface to be obtained, and, because of the large bulk of the supporting material, tends to reduce preferred orientation due to mechanical working of the sample and to packing of the particles. The patterns of the various dusts involved in a particular investigation are then recorded consecutively on the same length of strip chart, and at

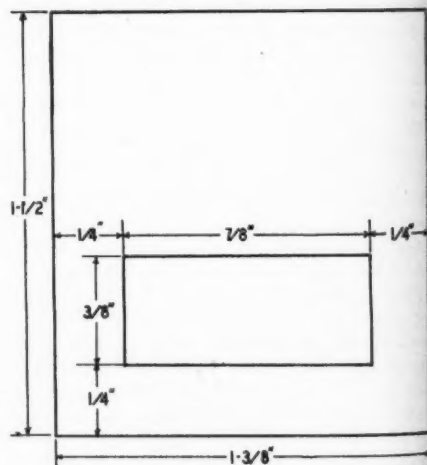


Fig. 3.

Sample slide. The slide is made of 1/16 inch thick aluminum sheet, and the sample cavity is backed by a glass cover slip.

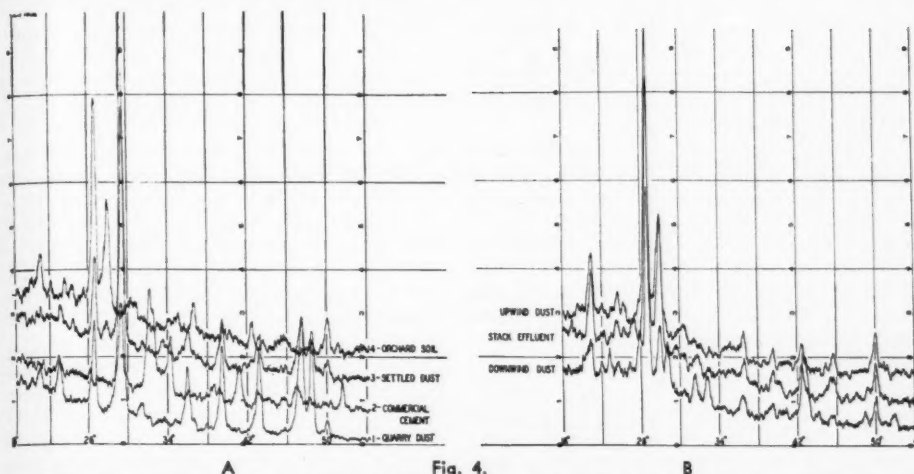


Fig. 4.

Diffraction pattern recordings showing background offset and method of comparative analysis. All patterns are precisely in phase and the background shift is accomplished by adjustment of the bias-bucking voltage supply. (A) Dust from cement plant and surroundings in rural area. (B) Dust from heavy industrialized urban area and surroundings.

identical instrument constants. The patterns are separated by applying either a bias or a bucking voltage to the potentiometer as the normal background produced by the sample dictates.

The use of this method of recording patterns and the type of studies made possible thereby are illustrated by two such studies recently completed. The first case concerns a cement plant in a rural area that was desirous of installing another kiln to augment the four it already had in operation. The residents of the immediate area became quite irate at this disclosure, and sought to have their governmental authorities withhold the necessary license. The company, of course, objected. The local health department was thrown into this impasse with instructions to uncover conclusive evidence on which the licensing board could act. Samples of settled dust were collected from the cement kilns of the plant and from the roofs and trees of complainants' property. Samples of soil from the immediate vicinity of the complainants' houses and of the cement company's quarry were also obtained. The samples were prepared and mounted as previously described and the diffraction patterns recorded as shown in Fig. 4A.

Inspection of commercial cement dust

pattern (2), shows major diffraction peaks at 2θ values of 32.3° , 37.4° , 41.2° , 47.0° , and 51.7° . Further inspection shows that these peaks do not occur in any of the other diffraction patterns. This is conclusive proof that the dust that settled on houses and trees in the areas under investigation was not cement dust and that the cement kiln operations were not responsible for the dusty conditions. There are, however, similarities between the quarry dust sample pattern (1), and the settled dust sample pattern (3), as well as between the settled dust sample pattern (3), and the orchard soil sample pattern (4). This indicates that the settled dust was a mixture of the orchard soil and the quarry dust. A comparison of the relative intensities of the similarities in patterns 1, 3, and 4 indicates that the quarry dust was the major constituent of the settled dust.

The second study illustrates more clearly how the contribution to the atmospheric dust of various plants in an area can be determined. In this case, the complainants, living in a heavily industrialized urban area, complained that a certain plant was producing a dusty condition, and sought to have this abated by appeals to the local district attorney. Again the health department was brought into the fray. Samples were collect-

ed in sootfall boxes at various locations surrounding the plant. Samples of dust from the plant itself also were collected. The diffraction patterns of these samples were recorded as shown in Fig. 4B.

In this comparison the downwind dust shows less similarity to the stack effluent than does the upwind dust. This appears to be an anomaly and would normally lead to a discrediting of the analytical results. In view of the high degree of specificity of x-ray diffraction patterns such discrediting was difficult and the solution of the paradox was sought elsewhere. Further field investigation disclosed the presence of a plant to windward of the location where the upwind samples were taken. Inquiry showed that this plant was using the same material as the plant under suspicion, and was producing a greater amount of dust. Closer examination of the diffraction pattern of the downwind sample shows two fairly prominent peaks at 25.8° and 32.7°. These peaks were identified as those of barite, (BaSO_4). Neither of the plants in question were using barite; however, it was found that a third plant adjacent to the plant originally under suspicion was engaged in the manufacture of barium salts and paint pigments, and that the raw material used was barite. Here, three plants were contributing to a dusty condition, but complaints were lodged against only one. The specificity of the x-ray diffraction patterns

and the ease with which they could be compared made it possible to institute proper and effective control measures, and to abate the nuisance.

IN CONCLUSION, it can be said that this method allows for the direct comparison of diffraction patterns with a minimum of confusion and a maximum of specificity. It makes it possible to determine the origin of atmospheric dusts by comparing the diffraction patterns of the airborne materials with the known plant effluent and does away with the necessity of preparing standard patterns or even determining the actual components of the material under study. The latter faculty is of utmost value, since the diffraction patterns of airborne dusts are often of such complexity as to defy identification. The graphic data and permanent record produced permit an objective analysis of situations often complicated with emotional and fallacious ideas. Finally, the specificity of the recorded data allows the field investigators to proceed with regulatory measures with a high degree of confidence.

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Errors Solicited

AN EXTENSIVE revision of "The Handbook of Dangerous Materials," by N. I. SAX (Rheinhold), is presently in process. Several new chapters are being prepared and the entire book is being critically reviewed and radically revised. For instance, to provide space for more entries, most extensive discussions will be deleted and each item will be presented with a straightforward statement of the type (chronic or acute), mode (inhalation, ingestion or contact), and degree of hazard. There is being presented, with each material, suggested means for controls consistent with the type and degree of hazard. These controls are individually keyed back to a chapter which discusses the application of control. There is a section on radiation safety, revised up to date, as well as an alphabetical listing and description of the commonly encountered radioisotopes. Finally, there will be chapters on fire, explosion and disaster hazards, keyed back to each item, as well as short sections on industrial sensitization and economic poisons. In the interest of increasing the value of the revision, MR. SAX urgently requests suggestions and comments regarding any error, either in fact or of omission, in the present volume. Any comment, or other type of criticism or suggestion will be welcome. Please address: N. I. SAX, 42-69 Phlox Place, Flushing 35, New York.

THE SALE OF

Uranium-Contaminated Scrap Carbon Steel TO COMMERCIAL CHANNELS

H. J. McALDUFF, Industrial Hygienist-Health Physicist
Atomic Energy Commission, Oak Ridge, Tennessee

THE sale and disposal of Government-owned radioactively contaminated metal, particularly that for which little or no need is anticipated in current or future programs, is a problem which has confronted the Atomic Energy Commission and its contractors almost since the beginning of operations.

The basic policy of the Commission, concerning the sale of contaminated property, was stated in a directive to all installations, dated February 10, 1947, subject: "Retention of Radioactive Property and Salvage Material." The first statement of the policy is quoted as follows: "It is essential that action be taken to prevent radioactive material from entering commercial channels. You will establish necessary procedures to insure that it is impossible for materials of this type to lose their identity or to enter commercial channels through sales or transfer of surplus property, salvage, and scrap."

The second statement of the policy defined the limits beyond which property and materials would be considered contaminated in terms of background and scale divisions of the radiation detection instruments then available. Difficulties were encountered in interpreting these values under field conditions, and in 1949 the Oak Ridge Operations Office restated the levels of contamination to its contracting organizations.

Property and materials exceeding the following maximum permissible levels of contamination would not be sold to commercial channels: (a) Alpha—500 disintegrations per minute per 100 square centimeters; and (b) Beta—gamma—0.04 mrep per hour in contact with the probe.

It will be recognized that these levels are well below the limits required for any known health considerations, and are such that essentially any detectable activity was sufficient to justify withholding the property or material from commercial channels. Also, at the time of these directives the extent of knowledge concerning the appropriate disposal of contaminated material was somewhat meager, and the amount of property which could be declared surplus to the overall effort was relatively small.

With the subsequent expansion of the Atomic Energy program in general, and in particular the dismantling of a portion of the electromagnetic processing equipment at the Y-12 Plant in Oak Ridge, the gross amounts of carbon steel, stainless steel, high alloy steel, and copper, contaminated to varying levels with depleted, normal, and enriched uranium, rapidly reached significant levels, creating in the process an acute storage problem at Y-12. The magnitude of this problem is illustrated by a conservative estimate of over 38,000 tons of carbon steel, alone, with an estimated market value of over \$1,000,000, that has and will be produced from the dismantling of this equipment.

This general problem was not confined to the Oak Ridge Operations Office. The New York Operations Office, experiencing somewhat similar difficulties, initiated a study to determine, if possible, the problems involved in releasing steel scrap contaminated with uranium through commercial scrap channels.

Briefly, the results of the study* indicate

Presented at the Radiation Session of the 15th Annual Meeting of the American Industrial Hygiene Association, Chicago, April 29, 1954.

*NYO-1558—"Investigation of the Potential Hazard in Releasing Scrap Steel Contaminated with Uranium to Commercial Channels" by Hanson Blatz, John H. Harley, Merrill Eisenbud.

that when steel scrap contaminated with uranium is smelted, the uranium apparently concentrates in the slag. Fluorometric analyses of samples of steel produced from smelting grossly-contaminated carbon steel indicated a uranium content of from 0.4 to 0.8 micrograms/gram of steel, as compared with a range of 0.01 to 0.2 micrograms/gram from samples of regular commercial steel produced prior to 1940. A sample of cast iron produced prior to 1940 contained 0.6 microgram of uranium per gram.

Further consideration of the health and industrial problems involved, which included obtaining the opinions of representatives of the photographic and radiation detection instrument industries with respect to the release of such scrap, led to the conclusion that these were not significant, and steps were taken in New York and Oak Ridge to initiate the disposal of contaminated ferrous scrap. It should be noted here that this action by the respective Operations' Offices was guided by the provisions of a Commission Bulletin issued in January, 1953 which stated, in effect, that the release of contaminated property should be subject to the approval of the Manager of Operations and to ICC regulations covering the shipment of such property. This bulletin was, to the best of my knowledge, the first modification to the original directive issued in 1947.

It was soon apparent that the initiation of procedures to provide for the disposal of the ferrous scrap at Oak Ridge was not so straight-forward as it had first seemed. Differences of opinion existed concerning levels of contamination which were considered appropriate for the release of such material. Legal questions were raised concerning proper notification to prospective purchasers of the nature of the material being offered, and appropriate language for the protection of the interests of the Commission and its contractors had to be derived for inclusion in the invitations to bid and terms and conditions of contracts of sale.

The most difficult problem, however, as far as Oak Ridge was concerned was the fact that some of the scrap which we proposed to sell was contaminated to varying degrees with enriched uranium. Although the actual quantities of enriched uranium

involved were considered negligible, and the disposal program certainly did not contemplate the release of any material containing significant quantities of enriched uranium; the very fact that the contamination was enriched (however slight the degree of enrichment) introduced a problem under the definition of "fissionable material" and other requirements of the Atomic Energy Act with respect to such materials.

Because of the nature of this problem, it became necessary to refer the task to the Washington level of Commission operations for appropriate action which was accordingly done. The efforts of the various Washington Divisions were augmented by the active cooperation of the Oak Ridge and New York Operations Offices, and resulted in the establishment of a Commission-wide policy with respect to the disposal of surface-uranium-contaminated ferrous metal scrap. The following provisions contained in the policy may be of interest:

1. **PURPOSE:** It is intended that disposal will be restricted to materials that have no value except for their basic material content.

2. **DISPOSAL CRITERIA:** Before disposal, all scrap proposed for sale shall be monitored using appropriate instruments and techniques, by qualified personnel of the AEC installation or AEC contractor conducting the disposal, to reasonably assure conformance to the specifications set forth. No scrap will be sold having an average alpha activity greater than 5000 disintegrations per minute per 100 square centimeters of surface or a peak alpha activity greater than 25,000 disintegrations per minute measured over 100 square centimeters of surface. In addition to the above limitations, there shall be no sale of scrap for which the average ratio of surface alpha activity to mass of scrap is greater than 10 disintegrations per minute per gram. The person monitoring the scrap shall sign and file a report stating his readings and observations and describing the lot of scrap involved. The scrap to be disposed of shall not include the following: (a) Materials having visible loose contamination; and (b) Containers, pipes, tubing, or machinery in which gross quantities of uranium-bearing materials can be entrapped and which cannot be checked by suitable monitoring techniques.

3. **APPLICABILITY OF THIS BULLETIN TO FERROUS METAL SCRAP SURFACE-CONTAMINATED WITH ENRICHED URANIUM:** The provisions of this Bulletin are equally applicable to ferrous metal scrap surface-contaminated with normal or enriched uranium.

4. **RAILWAY SHIPMENTS:*** Steel scrap may be shipped in railway gondola cars without reference to ICC regulations respecting the shipment of radioactive materials, providing that gamma radiation, measured above background, does not exceed 10 milliroentgens per 24 hours at any outside surface of the car.

It is considered that the policy and pro-

*This provision has been accepted as correct by a representative of the Bureau of Explosives.

cedures as established present a practical and realistic approach to the problem of disposing of such materials. It should be emphasized that these limits apply only to the sale of surface uranium contaminated carbon steel and do not apply to high alloy steels, stainless steel, copper and other metals. While it is realized that there are other contaminated materials that could be released without undue risk, additional modifications to the policy will only be made as experience is gained and as additional information is obtained. Toward this goal, work is continuing so that the large quantities of other scrap metals generated within Commission operations may be safely returned to commercial channels.

A Reminder

The Third National Air Pollution Symposium will be held at the Huntington-Sheraton Hotel in Pasadena, California, April 18-20, 1955.

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♦ President's Page

THE OFFICE of Executive Secretary has been capably handled by HENRY F. SMYTH for the past eight years. During this period, the only AIHA expense for office operation has been that for part-time secretarial help and the usual office supplies. Aside from the volunteer manpower, many facilities of the Mellon Institute have been made available.

It was previously reported here that DR. SMYTH has submitted his resignation, effective June 1, 1955. During the past nine months, the Officers and Board of Directors along with a number of special Committees, have been formulating details for changing the status of the Executive Secretary's office. Many members visualize the need for a full-time Executive Secretary. This seems impractical at present. A compromise part-time plan is being considered and will soon be submitted to the Board for approval.

Undoubtedly the period of transition will present many problems. Not the least of these will be financial. The Association has a surplus of approximately \$7000.00. This amount was accumulated prior to 1949. Since 1949, out-go has equaled income because of the increased cost of functioning, and the increased cost of QUARTERLY publication.

After June 1, 1955, there will be expenses above what have been normal for Association operation. These will include the salary of the new Executive Secretary, the purchase of certain office equipment, telephone, social security taxes, workmen's compensation insurance, and other incidental expenses which are impossible to determine now; the expense of publishing the reports of Technical Committees; and the cost of developing and expanding the QUARTERLY.

The Officers and Board of Directors have considered a number of possibilities for meeting the new financial obligations. They include: (1) Drawing on present reserves;



(2) Increasing membership dues; (3) Providing for Contributing Memberships; and (4) Providing for Industrial Memberships.

The first step taken to correct this unfavorable financial picture was to increase the QUARTERLY subscription rate effective January 1, 1955. This increase affected only non-member subscriptions. Member subscriptions are tied in with annual dues, and thus,

the total increase in 1955 income will be small.

An increase in membership dues and provision for membership classes require Constitutional or By-Law changes which must be introduced at an Annual Meeting and presented to the membership for acceptance or rejection. Assuming that the proposals made will be approved, we must wait until 1956 to realize a significant change in income.

USING present cash reserves is a practical approach for meeting financial obligations on a temporary basis, but some plan must be adopted to increase income if the Association is to survive. An increase in membership dues from the present \$6.00 seems essential. There is precedence in many technical societies for annual dues of \$15.00 and \$20.00 or more. However, it seems to be in the best interests of the organization that the annual dues be no more than \$10.00. If other membership classes are approved and are successful, the income from these sources should be sufficient to meet regular obligations and allow for reasonable expansion and growth.

When these proposals for meeting the present emergency are presented to the members, it is strongly urged that they be accepted. The small increased cost to each of us is little to pay for the rewards realized from a stronger professional organization, with greater recognition and prestige.

—HERBERT T. WALWORTH

♦ Selected Titles and Abstracts

—FROM FOREIGN EXCHANGE JOURNALS

THE FOLLOWING is a partial list of articles, by titles and authors, from journals received by the AMERICAN INDUSTRIAL HYGIENE ASSOCIATION since the December, 1954 issue of the Quarterly. Additional information on any of the journals or articles may be obtained from: CARROL S. WEIL, Senior Industrial Fellow, Mellon Institute of Industrial Research, 4400 Fifth Avenue, Pittsburgh 13.

I. THE JOURNAL OF SCIENCE OF LABOUR (Japan). Vol. 30, No. 6 (1954).

Studies on the Mutual Relation between Experimentally Produced Pulmonary Silicosis and Tuberculosis. Yoshibumi Ishii, pp. 347 to 367.

Some Findings on Chronic Xylol Poisoning. Tachio Hirokawa, pp. 381 to 389.

Painters exposed to concentrations of 100 to several hundred ppm of xylol in an enamel thinner composed of 40% xylol and 60% of gasoline were examined for 2½ years. An anemia of macrocytic type appeared which progressed with the duration of exposure. A tendency to leucopenia but no leucocytosis was found in both sexes.

II. THE JOURNAL OF SCIENCE OF LABOUR (Japan). Vol. 30, No. 7 (1954).

On Silicosis at a Certain Ceramic Factory in North Kyushu—the Effect of a Two-Year Enforcement of Antisilicosis Measures. Toichivo Sawada, Takeshi Nomura and Noriyuki Hirota, pp. 455 to 461.

Studies on Ear Defenders—On the Form of Ear Plugs. Mitsuo Morioka, pp. 462 to 464.

Japanese-manufactured ear plugs were considered inadequate in form and material. Trial models were prepared by molding the entrance of the external ear meatus with vinylpaste. They appear, states the author, excellent in elasticity and flexibility.

Studies on the Relation between the Constitution of the Flame of Welding and the Lead Content in the Environmental Air in a Storage Battery Industry. Naoyoshi Ida, Isamu Takata, Yoshimi Imamura and Yasuo Oki, pp. 471 to 474.

The lead content of the air in a storage battery factory was estimated by the impinger-polarographic method. The authors found that (1) the lead content of the air in a welding work room showed a marked increase by the use of a larger welding flame and (2) a simple mask that they devised to prevent exposure to

lead dust reduced the lead content of the air inside the mask to half that outside the mask.

III. LA MEDICINA DEL LAVORO (Italy). Vol. 45, No. 10 (1954).

Determination of the Anticholinesterase Activity and of the Maximum Tolerable Concentration in Atmospheres Contaminated by Organic Phosphorus Insecticides. N. Zurlo, C. Sassi and L. Mettrico, pp. 533 to 543.

The authors state it is difficult to accurately measure the atmospheric concentration of organic phosphorus insecticides as (a) the chemical composition of the compounds is variable, (b) the compounds are difficult to obtain in a *a priori* state and (c) their toxicity varies with the concentration of impurities. Therefore, preference was given to a biological determination of the anticholinesteric capacity of air in work-rooms. This consisted of measuring the inhibiting capacity on cholinesterase of 0.5 ml. of human serum which could saponify in one hour 0.05 millimol of acetylcholine in the conditions fixed by Morand and Laboris. The reduction of the cholinesterase is directly proportional to the atmospheric concentration. Having followed for three years personnel engaged in the preparation of Parathion the authors recommend that the MAC be set below a 5% reduction in the activity of 0.5 ml. of serum for exposures to Parathion. They suggest that the same value might apply to other organic phosphorus insecticides.

Book Review

INDUSTRIAL DUST—Second Edition: PHILIP I. DRINKER and THEODORE HATCH. Published by McGraw-Hill Book Company, New York, 1954, pp. 401, \$10.00.

The first edition of this book was published in 1936. It has served as a text and reference volume since its original publication on matters dealing with the effects of dust on man, and on methods and equipment related to the prevention and control of dust exposures. The original book as well as the revised edition was written by two outstanding authorities in the field of industrial hygiene.

The second edition of this book represents a careful revision of the subject matter. The number of pages of text has been increased from 276 to 346 and the number of chapters

has been increased from 14 to 17. The book content probably is best indicated by the chapter headings. These are: Physical Properties of Dust, Fumes, and Mists; Effects of Dusts and Fumes Upon Man; Inert and Toxic Dusts; Physical and Chemical Factors in Pneumoconiosis; Dust Retention by Man; The Dusty Trades; Appraisal of Dustiness; Determination of Dust Concentration (two chapters); Determination of Particle Size; Chemical and Mineralogical Analysis of Dust; Methods for the Control of Industrial Dust; Design of Local Exhaust Systems; Air Cleaning; Air Cleaning by Filtering; Scrubbing and Electrical Precipitation; and Dust Respirators and Air Masks.

The many new developments in the industrial hygiene of dusts, and the new concepts of the effects of certain dusts on man that have come into being since 1936 are discussed in this second edition. The substantial growth in knowledge as to the subject material necessitated rather thorough rewrites of most sections of the book. The increase in number of chapters does not mean that three new chapters have been added, but rather that the entire content of the book has been rearranged into 17 chapters and brought up to date. The increase in information on this subject since

the first edition was published is indicated by the increase in the number of references cited. The first edition contained 260 references to the literature and the second edition contains 458. A worthwhile addition to this book is a reference author index which includes the junior as well as the senior authors of all references cited.

The subjects discussed in this revised edition and not in the first one are many. Examples are: new methods of sampling, such as the thermal precipitator, cascade impactor, molecular filter and midjet impinger; the use of x-ray diffraction in analysis; new kinds of dust collectors, such as the reverse jet collector and the absolute filter; current concepts regarding silicosis; aluminum therapy for silicosis; and the inhalation effects of beryllium, arsenic, cadmium, selenium, tellurium, chromates, radioactive dusts, and insecticides.

The subject matter in this second edition of *INDUSTRIAL DUST* is well organized and presented. This book constitutes a valuable contribution to the literature in the field of industrial hygiene, especially as to the control of dust and its effects upon man. It will fill an important gap in the library of all industrial hygienists, and of others engaged in industrial hygiene work.

—ALLEN D. BRANDT

◆ *News of Local Sections*

Northern California Section

THE NORTHERN California Section held its regular meeting in Berkeley on January 11. DR. FRANCES R. HOLDEN spoke on the subject "Air Research at Stanford Research Institute." A meeting of the section was held March 8 in San Francisco. At this meeting DR. LESTER BRESLOW, Director of the Study of the Health Effects of Air Pollution, California State Department of Health, presented a preliminary report on the study carried out by his committee.

Michigan Section

V. K. ROWE, Dow Chemical Company, Biochemical Research Laboratories was guest speaker at a dinner meeting of the Michigan Industrial Hygiene Society held February 1. The meeting was held jointly with the Detroit Industrial Physicians Club. MR. ROWE's subject was "Problems of Health in Marketing of Chemicals."

Philadelphia Section

A MEETING of the Philadelphia Section was held January 11. DR. R. ECKARDT, Director, Medical Research Division, Esso Laboratories,

Standard Oil Development Company presented a paper entitled "Occupational Cancer." The speakers at the March 8 meeting were DR. W. A. EGGERT, Chief Psychologist, and A. H. MALT, Resident Psychologist, Lumbermens Mutual Casualty Insurance Company. Their subject was "Industrial Psychology in Industrial Hygiene and Safety."

Southern California Section

THE SOUTHERN California Section met in Hollywood February 24. The subject of the program was "Program and Research Problems in the Industrial Hygiene Division of the Health Department Agencies." Speakers were PAUL CAPLAN, California State Department of Health; JACK ROGERS, Los Angeles Health Department, and DR. MELVIN R. PLANCEY.

St. Louis Section

DR. JOSEPH F. TREON, Assistant Professor of Industrial Toxicology, University of Cincinnati addressed the St. Louis Section February 22. DR. TREON spoke on "Animal Investigations to Determine Safe Handling Requirements for Industrial Products."

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